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# ASYMPTOTIC BEHAVIOUR OF HIGHER FACTORIAL MOMENTS OF ELECTRON-PHOTON CASCADES AT LARGE DEPTHS

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In this paper the behaviour of the higher factorial moments of electron-photon cascades at large depths is investigated in approximation "A". The differential cross sections satisfying the conditions of homogeneity are positive, and, in addition, are arbitrary functions. It is assumed that the Bremsstrahlung cross section is greater than the pair formation cross section.

The main results of this paper are:

- 1) The main factor determining the development of the cascades at large depths is the product of the total number of particles and the threshold energy. Systems with a smaller value of this variable are privileged.
- 2) Photons, as primary particles, are "stronger" than electrons — generalization of the conclusions of Stachowiak (1956) for moments of any order.
- 3) Privileged configurations of electrons and photons were obtained. It turns out that configurations containing an even number of electrons different from zero are privileged. The weakest configuration for  $N$  particles is  $N$  photons and zero electrons when  $N > 1$ .

## § 1. Introduction

The object of this paper is to investigate the asymptotic relations satisfied by the higher factorial moments of electron-photon cascades for large depths. The problem is studied in the Approximation "A", i. e. the ionization losses being neglected. We assume that the cross sections satisfy the following conditions: 1) The differential cross section for the emission of a Bremsstrahlung photon per unit length has the form  $w^1(E/E_0) dE/E_0$

where  $E_0$  is the electron energy before the emission of a quantum

$E$  is the electron energy after the emission of a quantum

2) The differential cross section for electron-positron pair formation in a unit length has the form  $w^2(E/E_0) dE/E_0$

where  $E_0$  is the photon energy



$E$  is the energy of one of the electrons (i. e. an electron or positron) arising as a result of the reaction.

$$3) w^1(\varepsilon) w^2(\varepsilon) > 0 \text{ for } 0 < \varepsilon < 1$$

$$4) \int_0^1 w^1(\varepsilon) d\varepsilon = \alpha_1 > \int_0^1 w^2(\varepsilon) d\varepsilon = \alpha_2$$

We adopt the following notation:

A)  $q_{n,m}^i(\varepsilon_1 \dots \varepsilon_n; \varepsilon_{n+1} \dots \varepsilon_{n+m}; x) d\varepsilon_1 \dots d\varepsilon_{n+m}$  is the probability of finding at depth  $x$   $n$  electrons in the infinitesimal interval of energy  $(\varepsilon_i; \varepsilon_i + d\varepsilon_i)$  and  $m$  photons in the infinitesimal interval of energy  $(\varepsilon_k; \varepsilon_k + d\varepsilon_k)$ ,  $i = 1, 2, \dots, n$ ;  $k = n+1, \dots, n+m$  and any number of electrons and photons of any energy, if the primary particle is, for  $i = 1$ , an electron of unit energy and for  $i = 2$ , a photon of unit energy. The quantity  $q_{n,m}^i$  bears the name "product densities".

B)  $P^i(n, m|\varepsilon, x)$  is the probability of finding at depth  $x$   $n$  electrons and  $m$  photons of energy greater than  $\varepsilon$  and any number of electrons and photons of energy smaller than  $\varepsilon$ , if the primary particle is, for  $i = 1$ , an electron of unit energy, and, for  $i = 2$ , a photon of unit energy.

C)

$$S_{l,m}^i(\varepsilon, x) = l! m! \sum_{k=l}^{\infty} \sum_{n=m}^{\infty} \binom{k}{l} \binom{n}{m} P^i(k, n|\varepsilon, x)$$

is the factorial moment.

D)

$$G^i(\varepsilon, u_1, u_2, x) = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} P^i(n, m|\varepsilon, x) u_1^n u_2^m$$

is the generating function of the probabilities  $P^i(n, m|\varepsilon, x)$

Using notations A, B, C, D, we obtain the following relations:

$$S_{n,m}^i(\varepsilon, x) = \int_{\varepsilon}^1 d\eta_1 \dots \int_{\varepsilon}^1 d\eta_{n+m} q_{n,m}^i(\eta_1 \dots \eta_{n+m}; x) \quad (1.0)$$

(Messel and Potts 1952a)

$$P^i(n, m|\varepsilon, x) = \sum_{t=n+m}^{\infty} \frac{(-1)^{t+n+m}}{t!} \sum_{k=n}^{t-m} \left\{ \binom{t}{k} \binom{k}{n} \binom{t-k}{m} S_{k,t-k}^i(\varepsilon, x) \right\} \quad (1.1)$$

In deriving (1.1) we made use of the generally known properties of the generating function:

$$P^i(n, m|\varepsilon, x) = \frac{1}{n! m!} \left[ \frac{\partial^{n+m}}{\partial u_1^n \partial u_2^m} G^i(\varepsilon, u_1, u_2, x) \right]_{u_1=u_2=0}$$

$$S_{n,m}^i(\varepsilon, x) = \left[ \frac{\partial^{n+m}}{\partial u_1^n \partial u_2^m} G^i(\varepsilon, u_1, u_2, x) \right]_{u_1=u_2=1}$$

## § 2. Role of primary particles. Derivation of auxiliary relations

We make use of the fact shown by Urbanik (1956):

$$S_{n,k}^i(\varepsilon, x) = e^{-\alpha_2 x} V_{n,k}^i(\varepsilon, x)$$

$$\lim_{x \rightarrow \infty} e^{-\beta x} V_{n,k}^i(\varepsilon, x) = \begin{cases} 0 & \beta > 0 \\ \infty & \beta \leq 0 \end{cases} \quad (2.0)$$

We insert  $S_{n,k}^i$  written in the form above into the equation of the first collision for the moments (Janossy 1950)

$$\left[ \frac{\partial}{\partial x} + (\alpha_1 - \alpha_2) \right] V_{n,m}^i(\varepsilon, x) = \sum_{l=1}^{n-1} \sum_{k=1}^{m-1} e^{-\alpha_2 x} \int_0^1 w^i(\varepsilon') d\varepsilon' \left[ \binom{n}{l} \binom{m}{k} \times \right.$$

$$\times V_{l,m-k}^1\left(\frac{\varepsilon}{\varepsilon'}, x\right) V_{n-l,k}^{3-i}\left(\frac{\varepsilon}{1-\varepsilon'}, x\right) \Bigg] + \int_0^1 w^i(\varepsilon') d\varepsilon' \left[ V_{n,m}^1\left(\frac{\varepsilon}{\varepsilon'}, x\right) + \right.$$

$$\left. + V_{n,m}^{3-i}\left(\frac{\varepsilon}{1-\varepsilon'}, x\right) \right] \quad (2.1)$$

We divide on both sides by  $V_{n,m}^i$ . We pass to the limit and employ (2.0). The ratio  $\frac{\partial}{\partial x} V_{n,m}^i / V_{n,m}^i$  vanishes, since  $V_{n,m}^i$  tends to infinity more slowly than exponentially.

We obtain

$$(\alpha_1 - \alpha_2) = \lim_{x \rightarrow \infty} \int_0^1 w^i(\varepsilon') d\varepsilon' \left[ \frac{V_{n,m}^1\left(\frac{\varepsilon}{\varepsilon'}, x\right)}{V_{n,m}^i(\varepsilon, x)} + \frac{V_{n,m}^{3-i}\left(\frac{\varepsilon}{1-\varepsilon'}, x\right)}{V_{n,m}^i(\varepsilon, x)} \right]$$

And therefore:

$$0 = \lim_{x \rightarrow \infty} \int_0^1 w^2(\varepsilon') d\varepsilon' \frac{V_{n,m}^1\left(\frac{\varepsilon}{\varepsilon'}, x\right)}{V_{n,m}^2(\varepsilon, x)} \quad (2.2)$$

$$\alpha_1 - \alpha_2 = \lim_{x \rightarrow \infty} \int_0^1 w^1(\varepsilon') d\varepsilon' \left[ \frac{V_{n,m}^1\left(\frac{\varepsilon}{\varepsilon'}, x\right)}{V_{n,m}^1(\varepsilon, x)} + \frac{V_{n,m}^2\left(\frac{\varepsilon}{1-\varepsilon'}, x\right)}{V_{n,m}^1(\varepsilon, x)} \right] \quad (2.3)$$

Using the method given by Stachowiak for the first moments of the electron-photon cascade, we obtain, as a result of the fact that relations (2.2) and (2.3) are identical



with Stachowiak's relations, the following interesting relations:

$$\lim_{x \rightarrow \infty} \frac{V_{n,m}^1(\varepsilon, x)}{V_{n,m}^2(\varepsilon, x)} = \lim_{x \rightarrow \infty} \frac{S_{n,m}^1(\varepsilon, x)}{S_{n,m}^2(\varepsilon, x)} = 0 \quad (2.4)$$

$$\alpha_1 - \alpha_2 = \lim_{x \rightarrow \infty} \int_0^1 w^1(\varepsilon') d\varepsilon' \left\{ \frac{S_{n,m}^2\left(\frac{\varepsilon}{1-\varepsilon'}, x\right)}{S_{n,m}^1(\varepsilon, x)} \right\} \quad (2.5)$$

(Stachowiak 1956).

We now consider the conclusions resulting from the equation of the first collision for the product densities. This equation has the form

$$\begin{aligned} & \left( \frac{\partial}{\partial x} + \alpha_j \right) q_{n,m}^j(\vec{\eta}, x) \\ &= \sum_{\substack{k+l=n \\ p+s=m}}^* \int_0^1 w^i(\varepsilon) d\varepsilon \left[ q_{k,p}^1\left(\frac{\vec{\eta}}{\varepsilon}, x\right) q_{l,s}^{3-j}\left(\frac{\vec{\eta}''}{1-\varepsilon}, x\right) \right] \end{aligned} \quad (2.6)$$

In the notation used,  $\vec{\eta}$  is the set of variables  $(\eta_1 \dots \eta_n; \eta_{n+1} \dots \eta_{n+m})$ ;  $\eta|\varepsilon$  is the set of variables  $(\eta'_1|\varepsilon, \dots, \eta'_k|\varepsilon; \eta'_{k+1}|\varepsilon, \dots, \eta'_{k+p}|\varepsilon)$ ;  $\vec{\eta}''|1-\varepsilon$  is the set of variables  $(\eta''_1|1-\varepsilon, \dots, \eta''_l|1-\varepsilon; \eta''_{l+1}|1-\varepsilon, \dots, \eta''_{l+s}|1-\varepsilon)$ , where  $(\eta'_1 \dots \eta'_k, \eta''_1 \dots \eta''_l)$  are a permutation of the variables  $(\eta_1 \dots \eta_n)$ , and the variables  $(\eta'_{k+1} \dots \eta'_{k+p}, \eta''_{l+1} \dots \eta''_{l+s})$  are a permutation of  $(\eta_{n+1} \dots \eta_{n+m})$ . The summation sign with the asterisk denotes the summation not only over the indices, but also over all possible combinations  $(\eta'_1 \dots \eta'_k)$ ,  $(\eta''_1 \dots \eta''_l)$ , and all possible combinations  $(\eta'_{k+1} \dots \eta'_{k+p})$ ,  $(\eta''_{l+1} \dots \eta''_{l+s})$ . This equation is an application to the electron-photon cascade of the equation given by Messel (1952) for a nucleon cascade.

Using the formal analogy between equation (2.6) and Janossy's equation G, we can solve this equation formally for  $n+m > 1$  by employing the method given by Łopuszański (1952).

We obtain<sup>1)</sup>

$$\begin{aligned} q_{n,m}^i(\vec{\varepsilon}, x) &= \sum_{j=1}^2 \int_0^1 d\eta \int_0^1 \frac{d\omega}{\eta} \int_0^x d\xi \sum_{\substack{k+l=n \\ p+s=m}}^* w^j\left(\frac{\omega}{\eta}\right) \left( -\frac{\partial}{\partial \eta} S_{\delta_{1j}, \delta_{2j}}^i(\eta, x-\xi) \right) \times \\ &\quad \times q_{k,p}^1\left(\frac{\vec{\varepsilon}}{\omega}, \xi\right) q_{l,s}^{3-j}\left(\frac{\vec{\varepsilon}''}{\eta-\omega}, \xi\right) \end{aligned} \quad (2.7)$$

<sup>1</sup> In Eq. (2.7) and after  $\delta_{1f}$ ,  $\delta_{2f}$  is the Kronecker  $\delta$

The prime beside the summation sign denotes that expressions containing  $q_{n,m}^1$  and  $q_{n,m}^{3-j}$  should be omitted from the sum. We note that because of (1.0) and (2.0) the integrals

$$\int_0^\infty q_{k,p}^1(\vec{\eta}, x) q_{l,s}^{3-j}(\vec{\omega}, x) dx; \int_0^\infty q_{k,p}^1(\vec{\eta}, x) e^{a_2 x} q_{l,s}^{3-j}(\vec{\omega}, x) dx$$

will exist.

We shall estimate the ratio

$$q_{n,m}^i(\vec{\varepsilon}, x) \left/ \left( -\frac{\partial}{\partial \theta} S_{\delta_{if}, \delta_{if}}^k(\theta, x) \right) \right.$$

For this purpose we shall use equation (2.7) and a relation given by Urbanik (1956). On the basis of Urbanik's theorem, the function

$$e^{a_2(x-\xi)} \left( -\frac{\partial}{\partial \eta} S_{\delta_{ij}, \delta_{ij}}^i(\eta, x-\xi) \right) = v_j^i(\eta, x-\xi)$$

is a non-decreasing function of the variable  $(x-\xi)$ . Hence

$$v_j^i(\eta, x-\xi) \leq v_j^i(\eta, x)$$

Thus

$$\begin{aligned} \lim_{x \rightarrow \infty} \left[ q_{n,m}^i(\vec{\varepsilon}, x) \left/ \left( -\frac{\partial}{\partial \theta} S_{\delta_{if}, \delta_{if}}^k(\theta, x) \right) \right. \right] &\leq \lim_{x \rightarrow \infty} \sum_{j=1}^2 \int_0^1 d\eta \int_0^1 \frac{d\omega}{\eta} \left( \frac{\partial}{\partial \eta} S_{\delta_{ij}, \delta_{ij}}^i(\eta, x) \right) \times \\ &\times \left( \frac{\partial}{\partial \theta} S_{\delta_{if}, \delta_{if}}^k(\theta, x) \right)^{-1} \sum_{\substack{k+l=n \\ p+s=m}}^{*'} w_i \left( \frac{\omega}{\eta} \right) \int_0^\infty q_{k,p}^1 \left( \frac{\vec{\varepsilon}'}{\omega}, \xi \right) e^{a_2 \xi} q_{l,s}^{3-j} \left( \frac{\vec{\varepsilon}''}{\eta-\omega}, \xi \right) d\xi \end{aligned}$$

It is known that

$$q_{k,p}^1 \left( \frac{\vec{\varepsilon}'}{\omega}, \xi \right) = 0 \quad \text{if} \quad \frac{1}{\omega} \sum_{i=1}^{k+p} \varepsilon_i' > 1 \quad \text{and}$$

$$q_{l,s}^{3-j} \left( \frac{\vec{\varepsilon}''}{\eta-\omega}, \xi \right) = 0 \quad \text{if} \quad \frac{1}{\eta-\omega} \sum_{i=1}^{l+s} \varepsilon_i'' > 1$$

The product  $q_{k,p}^1 q_{l,s}^{3-j} = 0$  if either of the above inequalities occurs. If the inequality  $a_1 + a_2 > b_1 + b_2$  occurs, it follows, of course, that at least one of the inequalities  $a_1 > b_1$  or  $a_2 > b_2$  holds too; that is why the product  $q_{k,p}^1 q_{l,s}^{3-j}$  will equal zero if

$$\sum_{i=1}^{k+p} \varepsilon_i' + \sum_{i=1}^{l+s} \varepsilon_i'' > (\eta - \omega) + \omega = \eta$$



Since the set of variables  $(\varepsilon'_1 \dots \varepsilon'_k, \varepsilon''_1 \dots \varepsilon''_l)$  is a permutation of  $(\varepsilon_1 \dots \varepsilon_n)$  and the set  $(\varepsilon'_{k+1} \dots \varepsilon'_{k+p}, \varepsilon''_{l+1} \dots \varepsilon''_{l+s})$  a permutation of  $(\varepsilon_{n+1} \dots \varepsilon_{n+m})$ , then

$$\sum_{i=1}^{k+p} \varepsilon'_i + \sum_{i=1}^{l+s} \varepsilon''_i = \sum_{i=1}^{n+m} \varepsilon_i$$

and the condition for the product equalling zero can be replaced by

$$\sum_{i=1}^{n+m} \varepsilon_i > \eta \quad (2.9)$$

From the work of Konwent and Łopuszański (1956) it is known that

$$\lim_{x \rightarrow \infty} \left[ \left( \frac{\partial}{\partial \eta} S_{\delta_{ij}, \delta_{ij}}^i(\eta, x) \right) \middle/ \left( \frac{\partial}{\partial \theta} S_{\delta_{if}, \delta_{if}}^k(\theta, x) \right) \right] = 0 \quad \text{for } \eta > \theta$$

From the above and from (2.9) and (2.8) it follows that

$$\lim_{x \rightarrow \infty} \left[ q_{n,m}^i(\vec{\varepsilon}, x) \middle/ \left( \frac{\partial}{\partial \theta} S_{\delta_{if}, \delta_{if}}^k(\theta, x) \right) \right] = 0 \quad \text{for } \sum_{i=1}^{n+m} \varepsilon_i > \theta \quad (2.10)$$

We shall now estimate the ratio of  $q_{n,m}^i$  to the derivative with the respect to the energy of the first factorial moment in a somewhat different way. As known from the theorem of Urbanik, the derivative of the first factorial moment with respect to the energy tends to zero if  $x$  tends to infinity. Therefore we shall be able to choose a sequence  $\{x_s\}$  tending to infinity such that for every  $s$  we have

$$\left( -\frac{\partial}{\partial \eta} S_{\delta_{ij}, \delta_{ij}}^i(\eta, x_s) \right) \leq \left( -\frac{\partial}{\partial \eta} S_{\delta_{ij}, \delta_{ij}}^i(\eta, x_s - \xi) \right) \quad \text{for } 0 \leq \xi \leq x_s - \delta \quad (2.11)$$

$\delta > 0$

Relation (2.11) follows from the fact that the first derivative of the first moment with respect to the energy is the product of a decreasing non-positive function argument  $x$  and an exponential function different from zero at every point. We have

$$\begin{aligned} & \left[ q_{n,m}^i(\vec{\varepsilon}, x_s) \middle/ \left( -\frac{\partial}{\partial \theta} S_{\delta_{if}, \delta_{if}}^k(\theta, x_s) \right) \right] \\ & \geq \sum_{j=1}^2 \int_0^{x_s - \delta} d\xi \int_0^1 d\eta \int_0^1 \frac{d\omega}{\eta} \omega^j \left( \frac{\omega}{\eta} \right) \left( \frac{\partial}{\partial \eta} S_{\delta_{ij}, \delta_{ij}}^i(\eta, x_s - \xi) \right) \times \\ & \times \left( \frac{\partial}{\partial \theta} S_{\delta_{if}, \delta_{if}}^k(\theta, x_s) \right)^{-1} \sum_{\substack{k+l=n \\ p+s=m}}^* q_{k,p}^1 \left( \frac{\vec{\varepsilon}'}{\omega}, \xi \right) q_{l,s}^{3-j} \left( \frac{\vec{\varepsilon}''}{\eta - \omega}, \xi \right) \end{aligned}$$



Thus, from (2.11)

$$\begin{aligned} \lim_{s \rightarrow \infty} \left[ q_{n,m}^i(\vec{\varepsilon}, x_s) / \left( -\frac{\partial}{\partial \theta} S_{\delta_{1f}, \delta_{2f}}^k(\theta, x_s) \right) \right] &\geq \lim_{s \rightarrow \infty} \sum_{j=1}^2 \int_0^1 d\eta \int_0^1 \frac{d\omega}{\eta} \times \\ &\times w^j \left( \frac{\omega}{\eta} \right) \left( \frac{\partial}{\partial \eta} S_{\delta_{1j}, \delta_{2j}}^i(\eta, x_s) \right) \left( \frac{\partial}{\partial \theta} S_{\delta_{1j}, \delta_{2f}}^k(\theta, x_s) \right)^{-1} \sum_{\substack{k+l=n \\ p+s=m}}^{*'} \times \\ &\times \int_0^\infty q_{k,p}^1 \left( \frac{\vec{\varepsilon}'}{\omega}, \xi \right) q_{l,s}^{3-j} \left( \frac{\vec{\varepsilon}''}{\eta - \omega}, \xi \right) d\xi \end{aligned}$$

It is known that

$$q_{k,p}^1 \left( \frac{\vec{\varepsilon}'}{\omega}, \xi \right) \neq 0 \quad \text{if} \quad \sum_{i=1}^{k+p} \varepsilon_i' < \omega$$

$$\text{and } q_{l,s}^{3-j} \left( \frac{\vec{\varepsilon}''}{\eta - \omega}, \xi \right) \neq 0 \quad \text{if} \quad \sum_{i=1}^{l+s} \varepsilon_i'' \leq \eta - \omega$$

From the paper of Konwent and Łopuszański (1956) and from the definition of the sequence  $\{x_s\}$

$$\lim_{x \rightarrow \infty} \frac{\frac{\partial S_{\delta_{1f}, \delta_{2j}}^i(\eta, x)}{\partial \eta}}{\frac{\partial S_{\delta_{1f}, \delta_{2f}}^k(\theta, x)}{\partial \theta}} = \lim_{s \rightarrow \infty} \frac{\frac{\partial S_{\delta_{1j}, \delta_{2j}}^i(\eta, x_s)}{\partial \eta}}{\frac{\partial S_{\delta_{1f}, \delta_{2f}}^k(\theta, x_s)}{\partial \theta}} = \infty \text{ for } \eta < \theta$$

It is readily noted that only for

$$\theta > \sum_{i=1}^{k+p} \varepsilon_i' + \sum_{i=1}^{l+s} \varepsilon_i'' = \sum_{i=1}^{n+m} \varepsilon_i$$

will there exist on plane  $(\omega, \eta)$  a domain in which the product  $q_{k,p}^1 q_{l,s}^{3-j} \neq 0$  and the limit of the ratio of the derivatives with respect to the energy of the first moments both tend simultaneously to infinity. Thus, for

$$\theta > \sum_{i=1}^{n+m} \varepsilon_i \lim_{s \rightarrow \infty} \frac{q_{n,m}^i(\vec{\varepsilon}, x_s)}{\left( -\frac{\partial}{\partial \theta} S_{\delta_{1f}, \delta_{2f}}^k(\theta, x_s) \right)} = \infty$$

Because of the physical meaning of these quantities, this limit cannot depend on the choice of the sequence. Therefore

$$\lim_{x \rightarrow \infty} \left[ q_{n,m}^i(\vec{\varepsilon}, x) / \left( -\frac{\partial}{\partial \theta} S_{\delta_{1f}, \delta_{2f}}^k(\theta, x) \right) \right] = \infty \text{ for } \theta > \sum_{i=1}^{n+m} \varepsilon_i. \quad (2.13)$$

Dividing both sides of (2.10) by (2.13), we obtain

$$\lim_{x \rightarrow \infty} \frac{q_{n,m}^i(\vec{\varepsilon}, x)}{\left( -\frac{\partial S_{\delta_{1f}, \delta_{2f}}^k(\theta, x)}{\partial \theta} \right)} \times \lim_{x \rightarrow \infty} \frac{\left( -\frac{\partial}{\partial \theta} S_{\delta_{1f}, \delta_{2f}}^k(\theta, x) \right)}{q_{p,s}^j(\vec{\varepsilon}, x)} = 0$$

for  $\theta < \sum_{i=1}^{n+m} \varepsilon_i$  and for  $\theta > \sum_{i=1}^{p+s} \varepsilon'_i$ ; hence

$$\lim_{x \rightarrow \infty} \frac{q_{n,m}^i(\vec{\varepsilon}, x)}{q_{p,s}^j(\vec{\varepsilon}, x)} = 0 \text{ for } \sum_{i=1}^{n+m} \varepsilon_i > \sum_{i=1}^{p+s} \varepsilon'_i \quad (2.14)$$

### § 3. Conclusions from the equation of the last collision for product densities

We shall make use of a fact resulting from (1.0), (2.0), and (2.14). On the basis of these formulae, the function  $q_{n,m}^i$  can be represented in the form  $e^{-a_i x} Q_{n,m}^i(\vec{\varepsilon}, x)$ . The function  $Q_{n,m}^i(\vec{\varepsilon}, x)$  tends to infinity less slowly than exponentially. For this reason, we may assume

$$\lim_{x \rightarrow \infty} \frac{\frac{\partial}{\partial x} Q_{n,m}^i(\vec{\varepsilon}, x)}{Q_{n,m}^i(\vec{\varepsilon}, x)} = 0 \quad (3.0)$$

The equation of the last collision for the product densities (Messel and Potts, 1952b) has the form:

$$\left( \frac{\partial}{\partial x} + n \alpha_1 + m \alpha_2 \right) q_{n,m}^i(\varepsilon_1 \dots \varepsilon_n; \varepsilon_{n+1} \dots \varepsilon_{n+m}; x) = \sum_{C_i^N} q_{n-2, m+1}^i(\varepsilon'_1 \dots \varepsilon'_{n-2}; \varepsilon_{n+1} \dots \varepsilon_{n+m}; \varepsilon'_n + \varepsilon'_{n-1}; x) w^2 \left( \frac{\varepsilon'_n}{\varepsilon_n + \varepsilon_{n-1}} \right) \frac{1}{\varepsilon_n + \varepsilon_{n-1}} \quad (3.1A)$$

$$+ \sum_{C_i^N C_i^M} q_{n, m-1}^i(\varepsilon'_1 \dots \varepsilon'_{n-1}; \varepsilon'_n + \varepsilon'_{n+m}; \varepsilon'_{n+1} \dots \varepsilon'_{n+m-1}; x) w^1 \left( \frac{\varepsilon'_n}{\varepsilon_n + \varepsilon_{n+m}} \right) \frac{1}{\varepsilon_n + \varepsilon_{n+m}} \quad (3.1B)$$

$$+ \sum_{C_i^N} \int_0^1 q_{n,m}^i(\varepsilon'_1 \dots \varepsilon'_{n-1}, u; \varepsilon_{n+1} \dots \varepsilon_{n+m}; x) w^1 \left( \frac{\varepsilon'_n}{u} \right) \frac{du}{u} \quad (3.1C)$$

$$+ \sum_{C_i^M} \int_0^1 q_{n+1, m-1}^i(\varepsilon_1 \dots \varepsilon_n, u; \varepsilon'_{n+1} \dots \varepsilon'_{n+m-1}; x) w^1 \left( 1 - \frac{\varepsilon'_{n+m}}{u} \right) \frac{du}{u} \quad (3.1D)$$

$$+ \sum_{C_i^N} 2 \int_0^1 q_{n-1, m+1}^i(\varepsilon'_1 \dots \varepsilon'_{n-1}; \varepsilon_{n+1} \dots \varepsilon_{n+m}, u; x) w^2 \left( \frac{\varepsilon'_n}{u} \right) \frac{du}{u} \quad (3.1E)$$

## Notation:

Variables  $(\varepsilon'_1 \dots \varepsilon'_n)$  are a permutation of variables  $(\varepsilon_1 \dots \varepsilon_n)$

variables  $(\varepsilon'_{n+1} \dots \varepsilon'_{n+m})$  are a permutation of variables  $(\varepsilon_{n+1} \dots \varepsilon_{n+m})$

The summation signs with the indices 1)  $C_1^N$  2)  $C_1^M$ , 3)  $C_2^N$  denote, respectively, summation over all possible 1)  $\varepsilon'_n$ , 2)  $\varepsilon'_m$ , 3)  $\varepsilon'_n, \varepsilon'_{n-1}$  under the condition that if for  $\varepsilon'_n$  we take  $\varepsilon_k$ , then for  $\varepsilon'_{n-1}$  we can take only such  $\varepsilon_l$  for which  $l \neq k$ . We substitute into equation (3.1) the function  $q_{n,m}^i$  in the form of (3.0), after having taken into account the fact that  $w^i \left( \frac{\varepsilon'_n}{u} \right) = 0$  for  $u < \varepsilon'_n$  and  $w^1 \left( 1 - \frac{\varepsilon'_{n+m}}{u} \right) = 0$  for  $u < \varepsilon'_{n+m}$  and the obvious equality

$$\frac{q_{n,m}^i(\vec{\varepsilon}, x)}{q_{k,s}^i(\vec{\varepsilon}', x)} = \frac{Q_{n,m}^i(\vec{\varepsilon}, x)}{Q_{k,s}^i(\vec{\varepsilon}', x)}$$

we obtain  $n \alpha_1 + (m-1) \alpha_2 =$

$$= \sum_{C_1^N} \lim_{x \rightarrow \infty} \frac{q_{n-2,m+1}^i(\varepsilon'_1 \dots \varepsilon'_{n-2}; \varepsilon_{n+1} \dots \varepsilon_{n+m}, \varepsilon'_n + \varepsilon'_{n-1}; x)}{q_{n,m}^i(\varepsilon_1 \dots \varepsilon_n; \varepsilon_{n+1} \dots \varepsilon_{n+m}; x) [\varepsilon'_n + \varepsilon'_{n-1}]} w^2 \left( \frac{\varepsilon'_n}{\varepsilon'_n + \varepsilon'_{n-1}} \right) \quad (3.2A)$$

$$+ \sum_{C_1^N C_1^M} \lim_{x \rightarrow \infty} \frac{q_{n,m-1}^i(\varepsilon'_1 \dots \varepsilon'_{n-1}, \varepsilon'_n + \varepsilon'_{n+m}; \varepsilon_{n+1} \dots \varepsilon_{n+m-1}; x)}{q_{n,m}^i(\varepsilon_1 \dots \varepsilon_n; \varepsilon_{n+1} \dots \varepsilon_{n+m}; x) [\varepsilon'_n + \varepsilon'_{n+m}]} w^1 \left( \frac{\varepsilon'_n}{\varepsilon'_n + \varepsilon'_{n+m}} \right) \quad (3.2B)$$

$$+ \sum_{C_1^N} \lim_{x \rightarrow \infty} \int_{\varepsilon'_n}^1 \frac{q_{n,m}^i(\varepsilon'_1 \dots \varepsilon'_{n-1}, u; \varepsilon_{n+1} \dots \varepsilon_{n+m}; x)}{\varepsilon'_n q_{n,m}^i(\varepsilon_1 \dots \varepsilon_n; \varepsilon_{n+1} \dots \varepsilon_{n+m}; x)} w^1 \left( \frac{\varepsilon'_n}{u} \right) \frac{du}{u} + \quad (3.2C)$$

$$+ \sum_{C_1^M} \lim_{x \rightarrow \infty} \int_{\varepsilon'_{n+m}}^1 \frac{q_{m+1,m-1}^i(\varepsilon_1 \dots \varepsilon_n, u; \varepsilon'_{n+1} \dots \varepsilon'_{n+m-1}; x)}{q_{n,m}^i(\varepsilon_1 \dots \varepsilon_n; \varepsilon_{n+1} \dots \varepsilon_{n+m}; x)} w^1 \left( 1 - \frac{\varepsilon'_{n+m}}{u} \right) \frac{du}{u} \quad (3.2D)$$

$$+ \sum_{C_1^N} 2 \lim_{x \rightarrow \infty} \int_{\varepsilon'_n}^1 \frac{q_{n-1,m+1}^i(\varepsilon'_1 \dots \varepsilon'_{n-1}; \varepsilon_{n+1} \dots \varepsilon_{n+m}, u; x)}{q_{n,m}^i(\varepsilon_1 \dots \varepsilon_n; \varepsilon_{n+1} \dots \varepsilon_{n+m}; x)} w^2 \left( \frac{\varepsilon'_n}{u} \right) \frac{du}{u} \quad (3.2E)$$

Let us examine Eq. 3.2 for the particular case in which  $n = 0$ . It is readily noted that we shall have to discard the following terms:

(3.2A), (3.2B), (3.2D), (3.2E). We obtain

$$(m-1) \alpha_2 = \sum_{C_1^M} \lim_{x \rightarrow \infty} \int_{\varepsilon'_m}^1 \frac{q_{1,m-1}^i(u; \varepsilon'_1 \dots \varepsilon'_{m-1}; x)}{q_{0,m}^i(\varepsilon_1 \dots \varepsilon_m; x)} w^1 \left( 1 - \frac{\varepsilon'_m}{u} \right) \frac{du}{u}$$



For  $m \neq 1$  the side on the right must be different from zero. From (2.14):

$$\lim_{x \rightarrow \infty} \frac{q_{1,m-1}^i(u; \varepsilon_1' \dots \varepsilon_{m-1}'; x)}{q_{0,m}^i(\varepsilon_1' \dots \varepsilon_m'; x)} = 0 \quad \text{for } u + \sum_{i=1}^{m-1} \varepsilon_i' > \sum_{i=1}^m \varepsilon_i$$

Since  $\sum_{i=1}^m \varepsilon_i' = \sum_{i=1}^m \varepsilon_i$  the condition that

$$\lim_{x \rightarrow \infty} [q_{1,m-1}^i / q_{0,m}^i]$$

equal zero is replaced by  $\varepsilon_m' < u$ . Therefore, if we were to have

$$\lim_{x \rightarrow \infty} \frac{q_{1,m-1}^i(\varepsilon_m'; \varepsilon_1' \dots \varepsilon_{m-1}'; x)}{q_{0,m}^i(\varepsilon_1' \dots \varepsilon_m'; x)} \neq \infty$$

then the integral on the right would vanish and we would have  $(m-1)\alpha_2 = 0$ . Hence, for  $m > 1$  we have

$$\lim_{x \rightarrow \infty} \frac{q_{1,m-1}^i(\varepsilon_m'; \varepsilon_1' \dots \varepsilon_{m-1}'; x)}{q_{0,m}^i(\varepsilon_1' \dots \varepsilon_m'; x)} = \infty$$

From the paper of Konwent and Łopuszański it is known that for  $m = 1$  this limit is equal to zero. Therefore

$$\lim_{x \rightarrow \infty} \frac{q_{1,m-1}^i(\varepsilon_m; \varepsilon_1' \dots \varepsilon_{m-1}; x)}{q_{0,m}^i(\varepsilon_1' \dots \varepsilon_m; x)} = \frac{1 - \delta_{1m}}{\delta_{1m}} \quad (3.3)$$

Let us now pass on to the case in which  $n + m = 2$ . We note that by (2.14) the term (3.2C) vanishes. We now write the set of equations of the last collision for  $n + m = 2$ , taking into account the fact that (3.2C) vanishes with  $x$  going to infinity (Eq. (3.3)). From the equation for  $n = 0$  it follows, as previously (see (3.3)), that

$$\lim_{x \rightarrow \infty} \frac{q_{02}^i(\varepsilon_1, \varepsilon_2; x)}{q_{11}^i(\varepsilon_1; \varepsilon_2; x)} = 0$$

The remaining equations, after taking into account the above equation, have the form

$$\alpha_1 = \lim_{x \rightarrow \infty} \frac{q_{10}^i(\varepsilon_1 + \varepsilon_2; x)}{q_{11}^i(\varepsilon_1; \varepsilon_2; x)} w^1 \left( \frac{\varepsilon_1}{\varepsilon_1 + \varepsilon_2} \right) \frac{1}{\varepsilon_1 + \varepsilon_2} + \quad (3.4)$$

$$+ \lim_{x \rightarrow \infty} \int_{\varepsilon_2}^1 \frac{q_{20}^i(\varepsilon_1, u; x)}{q_{11}^i(\varepsilon_1; \varepsilon_2; x)} w^1 \left( 1 - \frac{\varepsilon_2}{u} \right) \frac{du}{u}$$

$$2\alpha_1 - \alpha_2 = \lim_{x \rightarrow \infty} \frac{q_{01}^i(\varepsilon_1 + \varepsilon_2; x)}{q_{20}^i(\varepsilon_1, \varepsilon_2; x)} w^2 \left( \frac{\varepsilon_1}{\varepsilon_1 + \varepsilon_2} \right) \frac{1}{\varepsilon_1 + \varepsilon_2} + \quad (3.5)$$

$$+ \sum_{C_1^N} 2 \lim_{x \rightarrow \infty} \int_{\varepsilon_2}^1 \frac{q_{11}^i(\varepsilon_1'; u; x)}{q_{20}^i(\varepsilon_1, \varepsilon_2; x)} w^2 \left( \frac{\varepsilon_2'}{u} \right) \frac{du}{u}$$

I denote by  $B_1$  the terms of equation (3.4) not under the integral sign and by  $B_2$  the terms of equation (3.5) not under the integral sign. The following cases are possible:

$$\text{Case 1. } B_1 = \alpha_1; \quad B_2 = 2\alpha_1 - \alpha_2$$

$$\text{Case 2. } B_1 < \alpha_1; \quad B_2 = 2\alpha_1 - \alpha_2$$

$$\text{Case 3. } B_1 = \alpha_1; \quad B_2 < 2\alpha_1 - \alpha_2$$

$$\text{Case 4. } B_1 < \alpha_1; \quad B_2 < 2\alpha_1 - \alpha_2$$

Let us consider them in turn.

Case 1. This case obviously is not in contradiction with the information in our possession, since from the fact the terms under the integral sign are equal to infinity at the boundary of the interval of integration we cannot come to any conclusions as to the value of the integral. Dividing on both sides the equalities defining Case 1, we obtain

$$\frac{\alpha_1 w^2 \left( \frac{\varepsilon_1}{\varepsilon_1 + \varepsilon_2} \right)}{(2\alpha_1 - \alpha_2) w^1 \left( \frac{\varepsilon_1}{\varepsilon_1 + \varepsilon_2} \right)} = \lim_{x \rightarrow \infty} \frac{\left\{ q_{10}^i(\varepsilon_1 + \varepsilon_2; x) \right\}}{\left\{ q_{01}^i(\varepsilon_1 + \varepsilon_2; x) \right\}} \frac{\left\{ q_{20}^i(\varepsilon_1, \varepsilon_2; x) \right\}}{\left\{ q_{11}^i(\varepsilon_1, \varepsilon_2; x) \right\}}$$

From the paper of Konwent and Łopuszański (1956) it is known that

$$\lim_{x \rightarrow \infty} \frac{q_{10}^i(\varepsilon, x)}{q_{01}^i(\varepsilon, x)} = 0$$

Therefore

$$\lim_{x \rightarrow \infty} \frac{q_{20}^i(\varepsilon_1, \varepsilon_2; x)}{q_{11}^i(\varepsilon_1, \varepsilon_2; x)} = \infty$$

Case 2. From the inequality defining Case 2 and from (3.4) we conclude that

$$\lim_{x \rightarrow \infty} \frac{q_{20}^i(\varepsilon_1, \varepsilon_2; x)}{q_{11}^i(\varepsilon_1, \varepsilon_2; x)} = \infty$$

Dividing the inequality in the definition of Case 2 on both sides, we conclude that  $\lim_{x \rightarrow \infty} \{q_{20}^i/q_{11}^i\}$  can be equal to infinity; therefore this is not a contradiction.

Case 3. From the inequality contained in the definition of Case 3 and from equation (3.5)

$$\lim_{x \rightarrow \infty} \frac{q_{11}^i(\varepsilon_1, \varepsilon_2; x)}{q_{20}^i(\varepsilon_1, \varepsilon_2; x)} = \infty$$

Dividing on both sides the inequality contained in the definition of this case by the equality contained in the definition of this case, we have

$$\lim_{x \rightarrow \infty} \frac{q_{20}^i(\varepsilon_1, \varepsilon_2; x)}{q_{11}^i(\varepsilon_1, \varepsilon_2; x)} = \infty$$

which leads to a contradiction.

Case 4. From (3.4) and from the definition of this case

$$\lim_{x \rightarrow \infty} \frac{q_{20}^i(\varepsilon_1, \varepsilon_2; x)}{q_{11}^i(\varepsilon_1, \varepsilon_2; x)} = \infty$$

From (3.5) and from the definition of this case

$$\lim_{x \rightarrow \infty} \frac{q_{11}^i(\varepsilon_1, \varepsilon_2; x)}{q_{20}^i(\varepsilon_1, \varepsilon_2; x)} = \infty$$

which leads to a contradiction.

Collecting the information from all the possible cases, we obtain

$$\lim_{x \rightarrow \infty} \frac{q_{11}^i(\varepsilon_1, \varepsilon_2; x)}{q_{20}^i(\varepsilon_1, \varepsilon_2; x)} = 0$$

In addition, from Cases 3 and 4 it follows that

$$\lim_{x \rightarrow \infty} \frac{q_{01}^i(\varepsilon_1 + \varepsilon_2; x)}{q_{20}^i(\varepsilon_1, \varepsilon_2; x)} = \frac{(2\alpha_1 - \alpha_2)(\varepsilon_1 + \varepsilon_2)}{w^2 \left( \frac{\varepsilon_1}{\varepsilon_1 + \varepsilon_2} \right)} \quad (3.6)$$

Employing (3.3) for  $m = 2$  we have

$$\lim_{x \rightarrow \infty} \frac{q_{02}^i(\varepsilon_1, \varepsilon_2; x)}{q_{11}^i(\varepsilon_1, \varepsilon_2; x)} = \lim_{x \rightarrow \infty} \frac{q_{11}^i(\varepsilon_1, \varepsilon_2; x)}{q_{20}^i(\varepsilon_1, \varepsilon_2; x)} = \lim_{x \rightarrow \infty} \frac{q_{02}^i(\varepsilon_1, \varepsilon_2; x)}{q_{20}^i(\varepsilon_1, \varepsilon_2; x)} = 0 \quad (3.7)$$

Doubtlessly, most interesting is the fact that the privileging of electrons for  $n + m = 2$  follows from the privileging of the photons for  $n + m = 1$ .

Dividing both sides of equality (3.6) by equality (3.6) taken for  $\varepsilon'_1$  and  $\varepsilon'_2$  such that  $\varepsilon'_1 + \varepsilon'_2 = \varepsilon_1 + \varepsilon_2$  we have

$$\lim_{x \rightarrow \infty} \frac{q_{20}^i(\varepsilon'_1, \varepsilon'_2; x)}{q_{20}^i(\varepsilon_1, \varepsilon_2; x)} = \frac{w^2 \left( \frac{\varepsilon'_1}{\varepsilon'_1 + \varepsilon'_2} \right)}{w^2 \left( \frac{\varepsilon_1}{\varepsilon_1 + \varepsilon_2} \right)}$$

which allows us to generalize relations (3.7). We have

$$\lim_{x \rightarrow \infty} \frac{q_{20}^i(\varepsilon'_1, \varepsilon'_2; x)}{q_{11}^i(\varepsilon_1, \varepsilon_2; x)} = \lim_{x \rightarrow \infty} \frac{q_{11}^i(\varepsilon'_1, \varepsilon'_2; x)}{q_{20}^i(\varepsilon_1, \varepsilon_2; x)} = \lim_{x \rightarrow \infty} \frac{q_{02}^i(\varepsilon'_1, \varepsilon'_2; x)}{q_{20}^i(\varepsilon_1, \varepsilon_2; x)} = 0 \quad (3.7')$$

If we investigate on the basis of (3.7) the equation for  $q_{n,m}^i$ ,  $n + m = 3$ , by a method analogous to the case of  $n + m = 2$ , we obtain the following relations:

$$\lim_{x \rightarrow \infty} \frac{q_{03}^i(\varepsilon_1, \varepsilon_2, \varepsilon_3; x)}{q_{12}^i(\varepsilon_1, \varepsilon_2, \varepsilon_3; x)} = \lim_{x \rightarrow \infty} \frac{q_{30}^i(\varepsilon_1, \varepsilon_2, \varepsilon_3; x)}{q_{21}^i(\varepsilon_1, \varepsilon_2, \varepsilon_3; x)} = \lim_{x \rightarrow \infty} \frac{q_{12}^i(\varepsilon_1, \varepsilon_2, \varepsilon_3; x)}{q_{21}^i(\varepsilon_1, \varepsilon_2, \varepsilon_3; x)} =$$



$$= \lim_{x \rightarrow \infty} \frac{q_{03}^i(\varepsilon_1, \varepsilon_2, \varepsilon_3; x)}{q_{21}^i(\varepsilon_1, \varepsilon_2; \varepsilon_3; x)} = \lim_{x \rightarrow \infty} \frac{q_{03}^i(\varepsilon_1, \varepsilon_2, \varepsilon_3; x)}{q_{30}^i(\varepsilon_1, \varepsilon_2, \varepsilon_3; x)} = 0. \quad (3.8)$$

$$\lim_{x \rightarrow \infty} \frac{q_{30}^i(\varepsilon_1, \varepsilon_2, \varepsilon_3; x)}{q_{12}^i(\varepsilon_1, \varepsilon_2, \varepsilon_3; x)} = \left\{ A(\varepsilon_1, \varepsilon_2, \varepsilon_3) \neq 0 \right\}$$

Proceeding similarly as in the case for  $n + m = 2$ , we arrive also at the relation:

$$\begin{aligned} 2\alpha_1 = & \lim_{x \rightarrow \infty} \frac{q_{02}^i(\varepsilon_3, \varepsilon_1 + \varepsilon_2; x)}{q_{21}^i(\varepsilon_1, \varepsilon_2; \varepsilon_3; x)} w^2 \left( \frac{\varepsilon_1}{\varepsilon_1 + \varepsilon_2} \right) \frac{1}{\varepsilon_1 + \varepsilon_2} + \\ & + \sum_{C_1^N} \lim_{x \rightarrow \infty} \frac{q_{20}^i(\varepsilon'_1, \varepsilon_3 + \varepsilon'_2; x)}{q_{21}^i(\varepsilon_1, \varepsilon_2; \varepsilon_3; x)} w^1 \left( \frac{\varepsilon'_2}{\varepsilon'_2 + \varepsilon_3} \right) \frac{1}{\varepsilon'_2 + \varepsilon_3} \end{aligned} \quad (3.9)$$

We transform this relation.

$$\begin{aligned} 2\alpha_1 = & \lim_{x \rightarrow \infty} \left\{ \frac{q_{02}^i(\varepsilon_3, \varepsilon_1 + \varepsilon_2; x)}{q_{21}^i(\varepsilon_1, \varepsilon_2; \varepsilon_3; x)} \right\} \left\{ w^2 \left( \frac{\varepsilon_1}{\varepsilon_1 + \varepsilon_2} \right) \frac{1}{\varepsilon_1 + \varepsilon_2} + \right. \\ & \left. + \sum_{C_1^N} \lim_{x \rightarrow \infty} \frac{q_{20}^i(\varepsilon'_1, \varepsilon'_2 + \varepsilon_3; x)}{q_{02}^i(\varepsilon_3, \varepsilon_1 + \varepsilon_2; x)} w^1 \left( \frac{\varepsilon'_2}{\varepsilon'_2 + \varepsilon_3} \right) \frac{1}{\varepsilon'_2 + \varepsilon_3} \right\} \end{aligned}$$

Because of (3.7) we have

$$\lim_{x \rightarrow \infty} \frac{q_{20}^i(\varepsilon'_1, \varepsilon'_2 + \varepsilon_3; x)}{q_{02}^i(\varepsilon_3, \varepsilon_1 + \varepsilon_2; x)} = \infty$$

from which we obtain

$$\lim_{x \rightarrow \infty} \frac{q_{02}^i(\varepsilon_3, \varepsilon_1 + \varepsilon_2; x)}{q_{21}^i(\varepsilon_1, \varepsilon_2; \varepsilon_3; x)} = 0.$$

Therefore

$$2\alpha_1 = \sum_{C_1^N} \lim_{x \rightarrow \infty} \frac{q_{20}^i(\varepsilon'_1, \varepsilon'_2 + \varepsilon_3; x)}{q_{21}^i(\varepsilon_1, \varepsilon_2; \varepsilon_3; x)} w^1 \left( \frac{\varepsilon'_2}{\varepsilon'_2 + \varepsilon_3} \right) \frac{1}{\varepsilon'_2 + \varepsilon_3} \quad (3.9')$$

From relations (3.8) it follows that the largest among  $q_{nm}^i$  for  $n + m = 3$  will be  $q_{21}^i$ , since, as may be seen from (3.8),

$$\lim_{x \rightarrow \infty} \frac{q_{k,3-k}^i(\varepsilon_1, \varepsilon_2, \varepsilon_3; x)}{q_{21}^i(\varepsilon_1, \varepsilon_2; \varepsilon_3; x)} = 0$$

for every  $k \neq 2$ ; ( $0 \leq k \leq 3$ ).

The next largest product densities will be  $q_{30}^i$  and  $q_{12}^i$  — their ratio at large depths tends to a finite value different from zero. It cannot be determined, by means of the methods used for estimation, which of these values is greater. This may depend on the specific values of the cross sections. The smallest among the  $q_{k,3-k}^i$  is  $q_{03}^i$ .

#### § 4. Conclusions from the relations obtained in § 1, 2, 3

$$\lim_{x \rightarrow \infty} \frac{\int_{\varepsilon_1}^1 d\eta_1 \dots \int_{\varepsilon_{n+m}}^1 d\eta_{n+m} q_{n,m}^i(\vec{\eta}, x)}{\int_{\varepsilon'_1}^1 d\eta'_1 \dots \int_{\varepsilon'_{p+s}}^1 d\eta'_{p+s} q_{p,s}^j(\vec{\eta}', x)} = \lim_{x \rightarrow \infty} \frac{\int_{\varepsilon_1}^1 d\eta_1 \dots \int_{\varepsilon_{n+m}}^1 d\eta_{n+m} \frac{q_{n,m}^i(\vec{\eta}, x)}{q_{n,m}^i(\vec{\varepsilon}, x)}}{\int_{\varepsilon'_1}^1 d\eta'_1 \dots \int_{\varepsilon'_{p+s}}^1 d\eta'_{p+s} \frac{q_{p,s}^j(\vec{\eta}', x)}{q_{n,m}^i(\vec{\varepsilon}, x)}} = 0$$

for  $\sum_{k=1}^{n+m} \varepsilon_k > \sum_{k=1}^{p+s} \varepsilon'_k$ , since, on the basis of (2.14), the numerator of the above fraction tends to zero and the denominator to infinity. For, in the region

$$\sum_{i=1}^{n+m} \varepsilon_i > \sum_{i=1}^{p+s} \eta'_i; \quad \eta'_i > \varepsilon'_i$$

which is contained in the domain of integration, we will have

$$\lim_{x \rightarrow \infty} \frac{q_{p,s}^j(\vec{\eta}', x)}{q_{n,m}^i(\vec{\varepsilon}, x)} = \infty$$

In particular, taking  $\varepsilon = \varepsilon_1 = \dots = \varepsilon_{n+m}$ ;  $\varepsilon' = \varepsilon'_1 = \dots = \varepsilon'_{p+s}$  and employing (1.0), we obtain

$$\lim_{x \rightarrow \infty} \frac{S_{n,m}^i(\varepsilon, x)}{S_{p,s}^j(\varepsilon', x)} = 0 \quad \text{for } (n+m)\varepsilon > \varepsilon'(p+s) \quad (4.0)$$

from which, for  $\varepsilon = \varepsilon'$ , we have

$$\lim_{x \rightarrow \infty} \frac{S_{n,m}^i(\varepsilon, x)}{S_{p,s}^j(\varepsilon, x)} = 0 \quad \text{for } (n+m) > (p+s) \quad (4.1)$$

In a second particular case:  $p+s = n+m = N$

$$\lim_{x \rightarrow \infty} \frac{S_{N-l,l}^i(\varepsilon, x)}{S_{N-k,k}^j(\varepsilon', x)} = 0 \quad \text{for } \varepsilon > \varepsilon' \quad (4.2)$$

From (1.1)

$$P^i(n, m | \varepsilon, x) = \frac{1}{(n+m)!} \sum_{k=n}^{(n+m)-m} \binom{n+m}{n} \binom{k}{n} \binom{n+m-k}{m} S_{k,n+m-k}^i(\varepsilon, x) \\ + R_{nm}[S_{k,l}^i(\varepsilon, x)] = \frac{1}{n!m!} S_{n,m}^i(\varepsilon, x) + R_{nm}[S_{k,l}^i(\varepsilon, x)]$$

where  $R_{nm}$  is a linear combination of the moments of an order higher than  $S_{n,m}^i$ ; and therefore, by (4.1), we will have

$$\lim_{x \rightarrow \infty} \frac{R_{nm} [S_{k,l}^i(\varepsilon, x)]}{S_{nm}^i(\varepsilon, x)} = 0$$

Thus, from the expression  $P^i(n, m | \varepsilon, x)$  and with the help of  $R_{nm}$  and  $S_{nm}^i$  we then obtain

$$\lim_{x \rightarrow \infty} \frac{\frac{1}{n! m!} S_{n,m}^i(\varepsilon, x)}{P^i(n, m | \varepsilon, x)} = 1 \quad (4.3)$$

By (4.3) and (4.0), we have

$$\lim_{x \rightarrow \infty} \frac{P^i(n, m | \varepsilon, x)}{P^j(p, s | \varepsilon, x)} = 0 \text{ for } (n + m) \varepsilon > \varepsilon' (p + s) \quad (4.4)$$

By a method similar to (4.0) and with the use of the mean value theorem, we shall show that if

$$\lim_{x \rightarrow \infty} \frac{q_{N-m,m}^i(\vec{\varepsilon}, x)}{q_{N-s,s}^j(\vec{\varepsilon}, x)} = 0$$

then also

$$\lim_{x \rightarrow \infty} \frac{S_{N-m,m}^i(\varepsilon, x)}{S_{N-s,s}^j(\varepsilon, x)} = 0$$

and if

$$\lim_{x \rightarrow \infty} \frac{q_{N-m,m}^i(\vec{\varepsilon}, x)}{q_{N-s,s}^j(\vec{\varepsilon}, x)} = \begin{cases} A(\vec{\varepsilon}) \neq 0 \\ \neq \infty \end{cases}$$

then we have

$$\lim_{x \rightarrow \infty} \frac{S_{N-m,m}^i(\varepsilon, x)}{S_{N-s,s}^j(\varepsilon, x)} = \begin{cases} B(\varepsilon) \neq 0 \\ \neq \infty \end{cases}$$

By using the relations obtained above, we have from (3.3)

$$\lim_{x \rightarrow \infty} \frac{S_{1,m-1}^i(\varepsilon, x)}{S_{0,m}^i(\varepsilon, x)} = \frac{1 - \delta_{1m}}{\delta_{1m}} \quad (4.5)$$

from (3.7)

$$\lim_{x \rightarrow \infty} \frac{S_{02}^i(\varepsilon, x)}{S_{11}^i(\varepsilon, x)} = \lim_{x \rightarrow \infty} \frac{S_{11}^i(\varepsilon, x)}{S_{20}^i(\varepsilon, x)} = \lim_{x \rightarrow \infty} \frac{S_{02}^i(\varepsilon, x)}{S_{20}^i(\varepsilon, x)} = 0 \quad (4.6)$$

from (3.8)

$$\lim_{x \rightarrow \infty} \frac{S_{03}^i(\varepsilon, x)}{S_{12}^i(\varepsilon, x)} = \lim_{x \rightarrow \infty} \frac{S_{30}^i(\varepsilon, x)}{S_{21}^i(\varepsilon, x)} = \lim_{x \rightarrow \infty} \frac{S_{12}^i(\varepsilon, x)}{S_{21}^i(\varepsilon, x)}$$



$$\begin{aligned}
&= \lim_{x \rightarrow \infty} \frac{S_{03}^i(\varepsilon, x)}{S_{21}^i(\varepsilon, x)} = \lim_{x \rightarrow \infty} \frac{S_{03}^i(\varepsilon, x)}{S_{30}^i(\varepsilon, x)} = 0 \\
&\lim_{x \rightarrow \infty} \frac{S_{30}^i(\varepsilon, x)}{S_{21}^i(\varepsilon, x)} = \left\{ \begin{array}{l} B(\varepsilon) \neq 0 \\ \neq \infty \end{array} \right\}
\end{aligned} \quad (4.7)$$

Employing (4.3), we obtain identical relations for the probabilities  $P^i(n, m | \varepsilon, x)$  and therefore

$$\lim_{x \rightarrow \infty} \frac{P^i(1, m-1 | \varepsilon, x)}{P^i(0, m | \varepsilon, x)} = \frac{1 - \delta_{1m}}{\delta_{1m}} \quad (4.5')$$

$$\lim_{x \rightarrow \infty} \frac{P^i(0, 2 | \varepsilon, x)}{P^i(1, 1 | \varepsilon, x)} = \lim_{x \rightarrow \infty} \frac{P^i(1, 1 | \varepsilon, x)}{P^i(2, 0 | \varepsilon, x)} = \lim_{x \rightarrow \infty} \frac{P^i(0, 2 | \varepsilon, x)}{P^i(2, 0 | \varepsilon, x)} = 0 \quad (4.6')$$

$$\begin{aligned}
&\lim_{x \rightarrow \infty} \frac{P^i(0, 3 | \varepsilon, x)}{P^i(1, 2 | \varepsilon, x)} = \lim_{x \rightarrow \infty} \frac{P^i(3, 0 | \varepsilon, x)}{P^i(2, 1 | \varepsilon, x)} = \lim_{x \rightarrow \infty} \frac{P^i(1, 2 | \varepsilon, x)}{P^i(2, 1 | \varepsilon, x)} \\
&= \lim_{x \rightarrow \infty} \frac{P^i(0, 3 | \varepsilon, x)}{P^i(2, 1 | \varepsilon, x)} = \lim_{x \rightarrow \infty} \frac{P^i(0, 3 | \varepsilon, x)}{P^i(3, 0 | \varepsilon, x)} = 0
\end{aligned} \quad (4.7')$$

$$\lim_{x \rightarrow \infty} \frac{P^i(3, 0 | \varepsilon, x)}{P^i(2, 1 | \varepsilon, x)} = \left\{ \begin{array}{l} B(\varepsilon) \neq 0 \\ \neq \infty \end{array} \right\}$$

Using a method similar to (3.6), we obtain

$$\lim_{x \rightarrow \infty} \frac{\int_{\varepsilon}^1 d\varepsilon_1 \int_{\varepsilon}^1 d\varepsilon_2 q_{01}^i(\varepsilon_1 + \varepsilon_2; x)}{S_{20}^i(\varepsilon, x)} = \lim_{x \rightarrow \infty} \frac{\int_{\varepsilon}^1 d\varepsilon_1 \int_{\varepsilon}^1 d\varepsilon_2 q_{20}^i(\varepsilon, \varepsilon_2; x) \left[ \frac{q_{01}^i(\varepsilon_1 + \varepsilon_2; x)}{q_{20}^i(\varepsilon_1, \varepsilon_2; x)} \right]}{S_{20}^i(\varepsilon, x)}$$

Making use of the mean value theorem in the integral in the numerator and employing (3.6) and (1.0), we obtain

$$\lim_{x \rightarrow \infty} \frac{\int_{\varepsilon}^1 d\varepsilon_1 \int_{\varepsilon}^1 d\varepsilon_2 q_{01}^i(\varepsilon_1 + \varepsilon_2; x)}{S_{20}^i(\varepsilon, x)} = \left\{ \begin{array}{l} \lambda(\varepsilon) \neq 0 \\ \neq \infty \end{array} \right\}$$

Let us consider the integral in the numerator. Form Abel's Theorem

$$R(\varepsilon) = \int_{\varepsilon}^1 d\varepsilon_1 \int_{\varepsilon}^1 d\varepsilon_2 q_{01}^i(\varepsilon_1 + \varepsilon_2; x) = 2 \int_{\varepsilon}^1 d\varepsilon_1 \int_{\varepsilon_1}^1 d\varepsilon_2 q_{01}^i(\varepsilon_1 + \varepsilon_2; x)$$

We employ a change of variables:  $\varepsilon_1 + \varepsilon_2 = \eta$ ;  $d\eta = d\varepsilon_2$ , and make use of (1.0). We have

$$R(\varepsilon) = 2 \int_{\varepsilon}^1 d\varepsilon_1 \int_{2\varepsilon_1}^1 d\eta q_{01}^i(\eta; x) = 2 \int_{\varepsilon}^1 d\varepsilon_1 S_{01}^i(2\varepsilon_1; x) = \int_{2\varepsilon}^1 S_{01}^i(\eta, x) d\eta$$

Also

$$\lim_{x \rightarrow \infty} \int_{2\varepsilon}^1 \frac{S_{01}^i(\eta, x)}{S_{20}^i(\varepsilon, x)} d\eta = \begin{cases} \lambda(\varepsilon) & \neq 0 \\ & \neq \infty \end{cases}$$

Since

$$\lim_{x \rightarrow \infty} \frac{S_{01}^i(\eta, x)}{S_{20}^i(\varepsilon, x)} = 0 \quad \text{for } \eta > 2\varepsilon \text{ (see 4.0)}$$

then, if we were to have

$$\lim_{x \rightarrow \infty} \frac{S_{01}^i(2\varepsilon, x)}{S_{20}^i(\varepsilon, x)} = C(\varepsilon) \neq \infty$$

we would therefore have

$$\lim_{x \rightarrow \infty} \int_{2\varepsilon}^1 \frac{S_{01}^i(\eta, x)}{S_{20}^i(\varepsilon, x)} d\eta = 0$$

Hence

$$\lim_{x \rightarrow \infty} \frac{S_{20}^i(\varepsilon, x)}{S_{01}^i(2\varepsilon, x)} = 0$$

From the above and from (4.6)

$$\lim_{x \rightarrow \infty} \frac{S_{2-k,k}^i(\varepsilon, x)}{S_{01}^i(2\varepsilon, x)} = 0; \quad 0 \leq k \leq 2 \quad (4.8)$$

We shall now obtain an analogous relation for  $n + m = 3$ . We transform relation (3.9'). As we know from § 3

$$\lim_{x \rightarrow \infty} \frac{q_{20}^i(\eta_1, \eta_2; x)}{q_{20}^i(\eta_1', \eta_2'; x)} \times \frac{w^2 \left( \frac{\eta_1'}{\eta_1' + \eta_2'} \right)}{w^2 \left( \frac{\eta_1}{\eta_1 + \eta_2} \right)} = 1 \quad (4.9)$$

$$\text{for } \eta_1' + \eta_2' = \eta_1 + \eta_2$$

Taking, in particular,

$$\eta_1' = \varepsilon_1'; \eta_2' = \varepsilon_2'; \eta_1 = \varepsilon_1 + \frac{1}{2} \varepsilon_3; \eta_2 = \varepsilon_2 + \frac{1}{2} \varepsilon_3$$

and multiplying every term of the sum in (3.9') by the left-hand side of the relation (4.9), we obtain

$$2\alpha_1 = \lim_{x \rightarrow \infty} \frac{q_{20}^i \left( \varepsilon_1 + \frac{1}{2} \varepsilon_3, \varepsilon_2 + \frac{1}{2} \varepsilon_3; x \right)}{q_{21}^i (\varepsilon_1, \varepsilon_2; \varepsilon_3; x)} \times \\ \times \sum_{C_1 N} \frac{w^1 \left( \frac{\varepsilon_2'}{\varepsilon_2' + \varepsilon_3} \right) w^2 \left( \frac{\varepsilon_1'}{\varepsilon_1 + \varepsilon_2 + \varepsilon_3} \right)}{w^2 \left( \frac{\varepsilon_1 + \frac{1}{2} \varepsilon_3}{\varepsilon_1 + \varepsilon_2 + \varepsilon_3} \right) [\varepsilon_2' + \varepsilon_3]}$$

From the above, as previously, we obtain

$$\lim_{x \rightarrow \infty} \frac{\int_{\varepsilon}^1 d\varepsilon_1 \int_{\varepsilon}^1 d\varepsilon_2 \int_{\varepsilon}^1 d\varepsilon_3 q_{20}^i \left( \varepsilon_1 + \frac{1}{2} \varepsilon_3, \varepsilon_2 + \frac{1}{2} \varepsilon_3; x \right)}{\int_{\varepsilon}^1 d\varepsilon_1 \int_{\varepsilon}^1 d\varepsilon_2 \int_{\varepsilon}^1 d\varepsilon_3 q_{21}^i (\varepsilon_1, \varepsilon_2; \varepsilon_3; x)} = \left\{ \mu(\varepsilon) \begin{array}{l} \neq 0 \\ \neq \infty \end{array} \right\}$$

Since

$$\int_{\varepsilon}^1 d\varepsilon_1 \int_{\varepsilon}^1 d\varepsilon_2 \int_{\varepsilon}^1 d\varepsilon_3 q_{20}^i \left( \varepsilon_1 + \frac{1}{2} \varepsilon_3, \varepsilon_2 + \frac{1}{2} \varepsilon_3; x \right) \\ = \int_{\varepsilon}^1 d\varepsilon_3 \int_{\varepsilon + \frac{1}{2} \varepsilon_3}^1 d\varepsilon_1 \int_{\varepsilon + \frac{1}{2} \varepsilon_3}^1 d\varepsilon_2 q_{20}^i (\varepsilon_1, \varepsilon_2; x) = \int_{\varepsilon}^1 d\eta S_{20}^i \left( \varepsilon + \frac{\eta}{2}, x \right)$$

then, as previously, we obtain

$$\lim_{x \rightarrow \infty} \frac{S_{20}^i \left( \frac{3}{2} \varepsilon, x \right)}{S_{21}^i (\varepsilon, x)} = \infty$$

from the above and from (4.7)

$$\lim_{x \rightarrow \infty} \frac{S_{3-k,k}^i (\varepsilon, x)}{S_{20}^i \left( \frac{3}{2} \varepsilon, x \right)} = 0; \quad 0 \leq k \leq 3$$

Then, from (4.8), for  $k = 0$ , we have

$$\lim_{x \rightarrow \infty} \frac{S_{3-k,k}^i (\varepsilon, x)}{S_{01}^i (3 \varepsilon, x)} = 0 \quad (4.10)$$



### Principle Results

1) The main factor governing the development of the cascade at large depths is the variable formed by the product of the total number of particles and the threshold energy. Systems with smaller values of this variable are privileged with respect to the systems with larger values of this variable. The primary particle and the qualitative composition of the cascade play a considerably smaller rôle these factors are only of importance when the two systems have the same value of the "main" variable.

In particular, for a fixed total number of particles the privileged systems are those with the smaller threshold energy; and for a fixed threshold energy, systems with a smaller number of particles.

2) At large depths the factorial moment  $S_{n,m}^i(\varepsilon x)$  tends to the  $n! m! P^i(n, m | \varepsilon, x)$ . This is a simple conclusion from 1).

3) The rôle of the primary particle. Stachowiak's conclusions have been generalized for moments of any order. Photons as a primary particle are "stronger". It has not proved possible to say anything about the limits of the ratios

$$\lim_{x \rightarrow \infty} \frac{S_{N-s,s}^1(\varepsilon, x)}{S_{N-k,k}^2(\varepsilon, x)}$$

such that

$$\lim_{x \rightarrow \infty} \frac{S_{N-s,s}^i(\varepsilon, x)}{S_{N-k,k}^i(\varepsilon, x)} = \infty$$

This is connected with the fact that in the theory two types of equations occur:

A) those with a fixed primary particle; in this case some different product densities for the highest total number of particles enter into the equations

B) those with a variable primary particle; only one product density for the highest total number of particles enters into these equations.

4) The role of the qualitative composition of the cascade. A privileged configuration of electrons and photons was obtained for  $n + m = 2$  and  $n + m = 3$ . One general conclusion was drawn for the probability of finding zero electrons and  $m$  photons, it having been shown that for large depths this probability is considerably smaller than the probability of finding  $m-1$  photons and one electron when  $m > 1$ .

### Interpretation of the Results

We should now interpret a result which at first glance seems to be paradoxical. This is the fact that the privileging of electrons for a total number of particles equal to two results from the photons being privileged for a total number of particles equal

to one. It is however quite clear that if one photon is "stronger" than the electron, then also the "decay products" of the first photon will be stronger than the decay products of the first electron. Thus, the two electrons that result from the "decay" of the photon will be stronger than the electron and the photon which are decay products of the electron by the radiation of a bremsstrahlung photon. It may be foreseen (as confirmed by more accurate calculations), that the "strongest" configuration of three particles will be two electrons and one photon, which are the result of the radiation of a photon by one of the two electrons of the most probable configuration of two particles.

As to the interpretation of relations (4.5) and (4.5'), this is also simple. The  $m$  photons ( $m > 1$ ) cannot arise from the configuration of  $m-1$  particles by a simple reaction, that is, the radiation of a single bremsstrahlung photon or the formation of one electron pair. This fact causes that the probability  $P^i(0, m | \varepsilon, x)$  is much smaller than  $P^i(1, m-1 | \varepsilon, x)$  for  $m > 1$ . On the basis of the examination of the influence of the qualitative composition of the cascade for two and three particles, the behaviour of the moments of higher order may be predicted.

It may be noted that the moments of order  $n + m > 1$  may be separated into three groups. Each moment  $S_{n,m}^i(\varepsilon, x)$  must belong to one and only one of the three groups. This follows from the simple fact, that if we consider a cascade consisting of exactly  $n$  electrons and  $m$  photons, this configuration can arise only by "simple reactions" either from primary electron or photon or at all can not arise in any way. By "simple reactions" we denote the transitions from occupation numbers  $(n, m)$  to  $(n+2, m-1)$  or from  $(n, m)$  to  $(n, m+1)$ . Thus, e. g. 2 electrons and 1 photon arise from the first photon by a sequence of simple reactions, since:

1 photon goes over into 2 electrons by pair formation

2 electrons go over into 2 electrons and 1 photon by the emission of a bremsstrahlung photon.

Two electrons and one photon cannot arise, e. g. from one electron and one photon by a sequence of simple reactions, since this configuration can go over into only two configurations of three particles:

3 electrons, and 1 electron and 2 photons.

The division of the factorial moments into groups according to the above criterion are:

1. Those arising from a single photon by a sequence of simple reactions,
2. Those arising from a single electron by a sequence of simple reactions
3. Those not being able to arise from any configurations of electrons and photons by a sequence of simple reactions — zero electrons and  $n + m$  photons for  $n + m > 1$ .

What belongs the moments of the same group, the ratio of moments for a fixed total number of particles and a fixed threshold energy will be tend, for large depths,

to a finite value different from zero and dependent on the specific value of the cross sections (which we did not consider in this paper).

The limit of the ratio of moments from different groups for the same fixed total number of particles and threshold energy will tend to zero if in the denominator there is a moment of smaller index.

There arises the question of whether explicit formulae for the configurations belonging to the 1st and 2nd groups cannot be given. It turns out that this can be done owing to the fact that the simple reactions, and hence also a sequence of them, do not change the parity of the electrons in the cascade. We thus conclude that to the 1st group can belong only configurations with an even number of electrons, and to the 2nd group, only configurations with an odd number of electrons. Since, as may readily be shown, every configuration of an even number of electrons different from zero can be obtained from one photon by a sequence of simple reactions, similarly as every configuration of an odd number of electrons can be obtained from a single electron by a sequence of simple reactions; then to the first group will belong all configurations which are even and which have a number of electrons greater than zero, and to the second group, all configurations with an odd number of electrons.

The properties given above of the division of the configurations of electrons and photons may, perhaps, seem doubtful. For purposes of explanation, we add that, independently of the possibility of a rigid proof (method of complete induction), the properties of the division given are based on a sufficiently clear physical fact, namely: if configuration A is "considerably stronger" than configuration B at large depths, then the decay products of configuration A will be "considerably stronger" than the decay products of configuration B. This physical fact corresponds mathematically to the fact that if configuration A' arises from configuration A, and configuration B' arises from B, where A is "considerably stronger" than B, then in the equation for the "product density" of configuration A' will be terms "considerably stronger" than the terms of the equation for the product density of configuration B'.

We shall now interpret relations (4.8) and (4.10). We assume that we have one photon above energy  $\varepsilon$ . On the basis of (4.2) we have a photon "infinitely close" to the threshold energy  $\varepsilon$ . We now assume that this photon decays into two electrons. Only in one case, for electron energies that are equal, does there exist the possibility of the production of 2 electrons of "infinitely close" energy  $\varepsilon/2$ . In all other cases we shall have only one electron above energy  $\varepsilon/2$ . This was the interpretation of (4.8); the interpretation of (4.10) is entirely similar.

In conclusion, I would like to thank Doc. Dr. Łopuszański, under whose direction this work was carried out, for suggesting the topic, for frequent consultations, and for critical remarks. It should also be mentioned that §2 of this paper is based on the generalization and application to the electron-photon cascade equations of a method given by Dr. Łopuszański for nucleon cascades.



## КРАТКОЕ СОДЕРЖАНИЕ

Г. Червонко, *Асимптотическое поведение высших факториальных моментов электронно-фотонных ливней на больших глубинах.*

В работе исследуется асимптотическое поведение на больших глубинах поглощения высших факториальных моментов электронно-фотонных ливней в аппроксимации „А”. Дифференциальные эффективные сечения — однородны и положительны — являются между тем произвольными функциями. При том, эффективное сечение на испускание фотонов торможения больше эффективного сечения на рождение электронно-позитронных пар.

Основные результаты:

1. Главный фактор решающий об поведении ливня на больших глубинах — это переменная равна произведению количества частиц на пороговую энергию. Система с меньшей „главной” переменной — вероятнее.
2. Фотоны, как первичные частицы — „сильнее” электронов; этой результат обобщение на моменты произвольного ранга результатов Стаховяка (1956).
3. Найдено привилегированные конфигурации системы из двух и трех частиц. Для двух частиц — это 2 электроны, для трех частиц — два электроны и один фотон.

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# A GENERAL EQUATION FOR SCATTERING AMPLITUDES OF PARTICLES IN THE FIELD THEORY

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In this note a formally exact relation in the field theory is obtained for the elements of the  $S$  matrix corresponding to two given numbers of particles. All elements with other numbers of particles are eliminated. Low's general equation derived in a previous paper (Królikowski, 1957) is a special case, when both distinguished numbers of particles are identical. If the two numbers of particles, say  $N_1$  and  $N_2$  are different, then the equation obtained here connects the transition  $N_1 \rightarrow N_2$  with the transition  $N_1 \rightarrow N_1$ , e. g. the photoproduction of pions with the Compton effect on nucleons. If the transition amplitude for the process  $N_1 \rightarrow N_1$  is known, then that for the process  $N_1 \rightarrow N_2$  satisfies a linear equation.

## 1. Introduction

We take into account a system of interacting fields having the total energy  $H$ . We assume that I) there exist states  $|\lambda(N)\rangle$  with definite numbers  $N$  of physical particles, representing asymptotic forms of scattering eigenstates of total energy of the system corresponding to the eigenvalues  $E_{\lambda(N)}$ :

$$(E_{\lambda(N)} - H) \Phi_{\lambda(N)}^{(\pm)} = 0,$$

$$\Phi_{\lambda(N)}^{(\pm)} = |\lambda(N)\rangle + \frac{1}{E_{\lambda(N)} - H \pm i\varepsilon} (H - E_{\lambda(N)}) |\lambda(N)\rangle \quad (1)$$

and II) the operators

$$\begin{aligned} U_N(E_{\lambda(N)}, W) &= P_N(H - E_{\lambda(N)}) P_N + U_N(W), \\ V_N^{(\pm)}(E_{\lambda(N)}) &= P_N(H - E_{\lambda(N)}) + V_N^{(\pm)} \end{aligned} \quad (2)$$

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are free from divergence (renormalization), where  $P_N$ ,  $U_N(W)$  and  $V_N^{(\pm)}$  are given by (5), (10) and (7), or (7'), respectively (Królikowski 1957)<sup>2</sup>

We denote by  $P_N$  the projection operator which acting on the state vector  $\Psi$  produces its component  $\Psi_N$  describing a given number  $N$  of physical particles. The projection operator  $P_{\perp N} = 1 - P_N$  acting on  $\Psi$  produces its component  $\Psi_{\perp N} = \Psi - \Psi_N$ .  $N$  is here (more strictly speaking) a given set of total numbers of physical particles corresponding to different fields under consideration. Using the orthogonal representation formed by vectors  $|\lambda(N)\rangle$ <sup>3</sup> we may write

$$P_N = \sum_{\lambda(N)} |\lambda(N)\rangle \langle \lambda(N)|, \quad P_{\perp N} = \sum_{N' \neq N} P_{N'}, \quad (5)$$

The eigenstates  $\Phi_{\lambda(N)}^{(+)}$  and  $\Phi_{\lambda(N)}^{(-)}$  of  $H$  containing outgoing and incoming waves, respectively, correspond to the initial conditions  $\Psi(t_0) = \Psi_N(t_0)$ , where  $t_0 \rightarrow -\infty$  and  $t_0 \rightarrow +\infty$ , respectively.

The time independent equation describing  $N$  physical particles (Królikowski 1957) has the form  $[\Psi_N^{(+)}(t) = \chi_N^{(+)} \exp(-iWt)]:$

$$(W - P_N H P_N - V_N^{(+)}) \chi_N^{(+)} = 0, \quad (6)$$

if  $\Psi(t_0) = \Psi_N(t_0)$  and  $t_0 \rightarrow -\infty$ . Here  $V_N^{(+)}$  is the interaction operator of  $N$  particles given by the equation

$$V_N^{(+)} = -i \int_0^{\infty} dt K_N(t) e^{i(P_N H P_N + V_N^{(+)})t} \quad (7)$$

<sup>2</sup> We note that if

$$H = \overset{0}{H} + \overset{1}{H}, \quad (3)$$

where

$$(E_{\lambda(N)} - \overset{0}{H}) |\lambda(N)\rangle = 0, \quad (4)$$

then

$$(H - E_{\lambda(N)}) |\lambda(N)\rangle = \overset{1}{H} |\lambda(N)\rangle.$$

We observe that if the conventional renormalization method is applicable  $\overset{0}{H}$  is then identical with the (renormalized) energy of free fields and  $\overset{1}{H}$  represents their (renormalized) interaction energy.

In the case of (3) the operators  $P_N$  and  $P_{\perp N}$  given by (5) commute with  $\overset{0}{H}$ . Thus we have  $\overset{0}{P}_N \overset{0}{H} \overset{0}{P}_N = \overset{0}{H} \overset{0}{P}_N$ ,  $\overset{0}{P}_{\perp N} \overset{0}{H} \overset{0}{P}_{\perp N} = \overset{0}{H} \overset{0}{P}_{\perp N}$  and  $[E_{\lambda(N)} - \overset{0}{P}_N \overset{0}{H} \overset{0}{P}_N] |\lambda(N)\rangle = 0$ .

<sup>3</sup> If the representation given by vectors  $|\lambda(N)\rangle$  were nonorthogonal, then we might define the operator  $P_N$  in (5) using two mutually contragradient systems of vectors (Królikowski 1957).



( $\hbar = 1$ ), where

$$K_N(t) = P_N H P_{\perp N} e^{-i P_{\perp N} H P_{\perp N} t} P_{\perp N} H P_N. \quad (8)$$

We have by virtue of (7) and (6)

$$V_N^{(+)} \chi_N^{(+)} = U_N(W) \chi_N^{(+)}, \quad (9)$$

where

$$U_N(W) = -i \int_0^\infty dt K_N(t) e^{i W t} = P_N H P_{\perp N} \frac{1}{W - P_{\perp N} H P_{\perp N} + i \varepsilon} P_{\perp N} H P_N. \quad (10)$$

For scattering states of  $N$  particles equation (6) takes the form (Królikowski 1957)

$$(E_{\lambda(N)} - P_N H P_N - V_N^{(+)}) \Phi_{\lambda(N)N}^{(+)} = 0 \quad (11)$$

and hence

$$\Phi_{\lambda(N)N}^{(+)} = |\lambda(N)\rangle + \frac{1}{E_{\lambda(N)} - P_N H P_N - V_N^{(+)} + i\varepsilon} V_N^{(+)}(E_{\lambda(N)}) |\lambda(N)\rangle, \quad (12)$$

where  $V_N^{(+)}(E_{\lambda(N)})$  is given by (2). Here the solution  $\Phi_{\lambda(N)N}^{(+)}$  of (11) is the component describing  $N$  particles of the eigenstate  $\Phi_{\lambda(N)}^{(+)}$  of  $H$ :

$$\Phi_{\lambda(N)N}^{(+)} = P_N \Phi_{\lambda(N)}^{(+)}. \quad (13)$$

Note that from the first equation (1) we obtain

$$P_{\perp N} \Phi_{\lambda(N)}^{(+)} = \frac{1}{E_{\lambda(N)} - P_{\perp N} H P_{\perp N} + i\varepsilon} P_{\perp N} H P_N \Phi_{\lambda(N)}^{(+)}, \quad (14)$$

if we consider a process for which the system is initially in a state of  $N$  particles:  $\Psi(t_0) = \Psi_N(t_0)$  and  $t_0 \rightarrow -\infty$ .

## 2. The $S$ Matrix

The elements of the  $S$  matrix for transitions  $\lambda(N_1) \rightarrow \lambda'(N_2)$  may be represented in the form (cf. Lippmann and Schwinger 1950, Gell-Mann and Goldberger 1953, Eckstein 1956, Eckstein and Tanaka 1956)

$$\langle \lambda'(N_2) | S | \lambda(N_1) \rangle = \delta_{\lambda'(N_2)\lambda(N_1)} - 2\pi i \delta(E_{\lambda'(N_2)} - E_{\lambda(N_1)}) T_{\lambda'(N_2)}^{(+)}(\lambda(N_1)), \quad (15)$$

where

$$T_{\lambda'(N_2)}^{(+)}(\lambda(N_1)) = \langle \lambda'(N_2) | (H - E_{\lambda'(N_2)}) \Phi_{\lambda(N_1)}^{(+)} \rangle. \quad (16)$$

Formula (16) for scattering amplitudes — owing to (14) — may be rewritten as follows

$$\begin{aligned} T_{\lambda'(N_2)}^{(+)}(\lambda(N_1)) &= \langle \lambda'(N_2) | [P_{N_2}(H - E_{\lambda'(N_2)}) P_{N_1} + P_{N_2}(H - E_{\lambda'(N_2)}) P_{\perp N_1}] \Phi_{\lambda(N_1)}^{(+)} \rangle = \\ &= \langle \lambda'(N_2) | U_{N_2 N_1}(N_1, E_{\lambda'(N_2)}, E_{\lambda(N_1)}) \Phi_{\lambda(N_1) N_1} \rangle = \\ &= \langle \lambda'(N_2) | V_{N_2 N_1}^{(+)}(N_1, E_{\lambda'(N_2)}) \Phi_{\lambda(N_1) N_1} \rangle, \end{aligned} \quad (17)$$

where

$$\begin{aligned} U_{N_2 N_1}(N_1, E_{\lambda(N_2)}, W) &= \\ P_{N_2} \left[ H - E_{\lambda(N_2)} + (H - E_{\lambda(N_2)}) P_{\perp N_1} \frac{1}{W - P_{\perp N_1} H P_{\perp N_1} + i\varepsilon} P_{\perp N_1} H \right] P_{N_1} &= \\ P_{N_2}(H - E_{\lambda(N_2)}) P_{N_1} - i \int_0^\infty dt K_{N_2 N_1}(N_1, E_{\lambda(N_2)}, t) e^{iWt}, \end{aligned} \quad (18)$$

$$V_{N_2 N_1}(N_1, E_{\lambda(N_2)}) = P_{N_2}(H - E_{\lambda(N_2)}) P_{N_1} - i \int_0^\infty dt K_{N_2 N_1}(N_1, E_{\lambda(N_2)}, t) e^{i(P_{N_1} H P_{N_1} + V_{N_1}^{+})t} \quad (19)$$

and

$$K_{N_2 N_1}(N_1, E_{\lambda(N_2)}, t) = P_{N_2}(H - E_{\lambda(N_2)}) P_{\perp N_1} e^{-iP_{\perp N_1} H P_{\perp N_1} t} P_{\perp N_1} H P_{N_1} \quad (20)$$

Here by virtue of (6)

$$V_{N_2 N_1}^{(+)}(N_1, E_{\lambda(N_2)}) \chi_{N_1}^{(+)} = U_{N_2 N_1}(N_1, E_{\lambda(N_2)}, W) \chi_{N_1}^{+}. \quad (21)$$

Note that

$$\begin{aligned} U_N(E_{\lambda(N)}, W) &= U_{NN}(N, E_{\lambda(N)}, W), \quad V_N^{(+)} = V_{NN}^{+}(N, E_{\lambda(N)}), \\ K_N(t) &= K_{NN}(E_{\lambda(N)}, t). \end{aligned} \quad (22)$$

From (17) and (12) we obtain

$$\begin{aligned} T_{\lambda'(N_2)}^{(+)}(\lambda(N_1)) &= \langle \lambda'(N_2) | V_{N_2 N_1}^{(+)}(N_1, E_{\lambda'(N_2)}) | \lambda(N_1) \rangle + \\ &+ \langle \lambda'(N_2) | V_{N_2 N_1}^{(+)}(N_1, E_{\lambda'(N_2)}) \frac{1}{E_{\lambda(N_1)} - P_{N_1} H P_{N_1} - V_{N_1}^{(+)} + i\varepsilon} V_{N_1}^{(+)}(E_{\lambda(N_1)}) | \lambda(N_1) \rangle \end{aligned} \quad (23)$$

Assuming that the vectors  $\Phi_{\lambda(N)N}^{(+)}$ ,  $\chi_{NbN}^{(+)}$ ,  $(\chi_{NbN}^{+})$  are bound states of  $N$  particles or scattering on bound states) form a complete system in the subspace of  $N$  particles and taking into account the contragradient system of vectors  $\Phi_{N}^{(+)\lambda(N)}$ ,  $\chi_N^{(+)\lambda(N)}$  [because here the system of eigenstates of (6) affords in general a non-orthogonal basis; the "potentials"  $V_N^{(+)}$  is complex; (Królikowski 1957)], we obtain

$$\begin{aligned} T_{\lambda'(N_2)}^{(+)}(\lambda(N_1)) &\equiv \langle \lambda'(N_2) | V_{N_2 N_1}^{(+)}(N_1, E_{\lambda'(N_2)}) \Phi_{\lambda(N_1) N_1}^{(+)} \rangle \\ &= \langle \lambda'(N_2) | V_{N_2 N_1}^{(+)}(N_1, E_{\lambda'(N_2)}) | \lambda(N_1) \rangle + \end{aligned}$$

$$\begin{aligned}
 & + \sum_{\lambda''(N_1)} \frac{\langle \lambda'(N_2) | V_{N_2 N_1}^{(+)}(N_1, E_{\lambda'(N_2)}) \Phi_{\lambda''(N_1) N_1}^{(+)} \langle \Phi^{(+)\lambda''(N_1)} V_{N_1 N_1}^{(+)}(N_1, E_{\lambda(N_1)}) | \lambda(N_1) \rangle}{E_{\lambda(N_1)} - E_{\lambda''(N_1)} + i\varepsilon} \\
 & + \sum_{b_{N_1}} \frac{\langle \lambda'(N_2) | V_{N_2 N_1}^{(+)}(N_1, E_{\lambda(N_2)}) \chi_{N_1 b_{N_1}}^{(+)} \langle \chi_{N_1}^{(+)\lambda(N_1)} V_{N_1 N_1}^{(+)}(N_1, E_{\lambda(N_1)}) | \lambda(N_1) \rangle}{E_{\lambda(N_1)} - \bar{E}_{b_{N_1}} + i\Gamma_{b_{N_1}} + i\varepsilon} \quad (24)
 \end{aligned}$$

( $\bar{W}_{b_N} = E_{b_N} - i\Gamma_{b_N}$ ). Equation (24) forms a simultaneous system of equations together with the equation in which the roles of the lower and upper labels of  $\Phi^{(+)}$  and  $\chi^{(+)}$  are interchanged and  $V^{(+)*}$  appears instead of  $V^{(+)}$  (and  $-i\Gamma_b$  instead of  $+i\Gamma_b$ ) (Królikowski 1957).

If the imaginary parts of the operators  $V_{N_2 N_1}^{(+)}(N_1)$  and  $V_{N_1 N_1}^{(+)}(N_1)$  are so "small" that their influence may be neglected in the numerators of (24), then equation (24) takes the following approximative form

$$\begin{aligned}
 T_{\lambda'(N_2)}^{(+)}(\lambda(N_1)) &= \langle \lambda'(N_2) | V_{N_2 N_1}^{(+)}(N_1, E_{\lambda'(N_2)}) | \lambda(N_1) \rangle + \\
 & + \sum_{\lambda''(N_1)} \frac{T_{\lambda'(N_2)}^{(+)} \lambda''(N_1) T_{\lambda(N_1)}^{(+)*}(\lambda''(N_1))}{E_{\lambda(N_1)} - E_{\lambda(N_1)} + i\varepsilon} + \\
 & + \sum_{b_{N_1}} \frac{\langle \lambda'(N_2) | V_{N_2 N_1}^{(+)}(N_1, E_{\lambda'(N_2)}) \chi_{N_1 b_{N_1}}^{(+)} \langle \lambda(N_1) | V_{N_1 N_1}^{(+)}(N_1, E_{\lambda(N_1)}) \chi_{N_1 b_{N_1}}^{(+)*} \rangle}{E_{\lambda(N_1)} - \bar{E}_{b_{N_1}} + i\Gamma_{b_{N_1}} + i\varepsilon} \quad (25)
 \end{aligned}$$

In (24) and (25) the first term on the r.h.s. represents the Born approximation for the transition  $\lambda(N_1) \rightarrow \lambda'(N_2)$  with the exact "interaction" operator  $V_{N_2 N_1}^{(+)}(N_1, E_{\lambda'(N_2)})$  of  $N_1$  particles with  $N_2$  particles. For  $N_1 = N_2$  both equations pass over into the corresponding equations (Królikowski 1957).

In the case  $N_1 \neq N_2$  the equation (25) would be linear with respect to  $T_{\lambda'(N_2)}^{(+)}(\lambda(N_1))$  if  $T_{\lambda'(N_1)}^{(+)}(\lambda(N_1))$  were known. For  $T_{\lambda'(N_1)}^{(+)}(\lambda(N_1))$  we have another (non-linear) equation (the one given in paper (Królikowski 1957)), which arises from (25) when we put  $N_2 = N_1$ . This equation does not contain scattering amplitudes other than  $T_{\lambda'(N_1)}^{(+)}(\lambda(N_1))$ . For example the latter equation may be that for the scattering of photons on nucleons ( $\gamma + N \rightarrow \gamma + N$ ) and the former may describe photoproduction of pions ( $\gamma + N \rightarrow \pi + N$ ). In this example  $N_1 = (1 \text{ photon}, 1 \text{ nucleon})$ ,  $N_2 = (1 \text{ pion}, 1 \text{ nucleon})$  and  $T_{\lambda'(N_2)}^{(+)}(\lambda(N_1))$  describes photoproduction of pions, whereas  $T_{\lambda'(N_1)}^{(+)}(\lambda(N_1))$  is due to the Compton effect on nucleons.

### Acknowledgement

I am extremely indebted to Professor W. Pauli and Professor R. Jost for the hospitality in E. T.H. in Zürich and for the helpful discussions.

## Appendix

The elements of the  $S$  matrix for transitions  $\lambda(N_1) \rightarrow \lambda'(N_2)$  may be also represented by

$$\langle \lambda'(N_2) | S | \lambda(N_1) \rangle = \delta_{\lambda'(N_2)\lambda(N_1)} - 2\pi i \delta(E_{\lambda'(N_2)} - E_{\lambda(N_1)}) T_{\lambda(N_1)}^{(-)}(\lambda'(N_2)) \quad (15')$$

(instead of (15)), where

$$T_{\lambda(N_1)}^{(-)}(\lambda'(N_2)) = \langle \Phi_{\lambda'(N_2)}^{(-)}(H - E_{\lambda(N_1)}) | \lambda(N_1) \rangle \quad (16')$$

(instead of (16)). The amplitudes (16) and (16') are, in general, equal only on the energy shell.

The eigenstates  $\Phi_{\lambda(N)}^{(-)}$  of  $H$  containing incoming waves correspond to the initial condition:  $\Psi(t_0) = \Psi_N(t_0)$  and  $t_0 \rightarrow +\infty$ . Then the time-independent equation describing  $N$  physical particles has (instead of (6)) the form

$$[\Psi_N^{(-)}(t) = \chi_N^{(-)} \exp(-iW^*t)]:$$

$$(W^* - P_N H P_N - V_N^{(-)*}) \chi_N^{(-)} = 0, \quad (6')$$

where  $V_N^{(-)*}$  is the Hermitian conjugate of  $V_N^{(-)}$ , that is now defined by the equation (instead of (7))

$$V_N^{(-)} = -i \int_0^\infty dt e^{i(P_N H P_N + V_N^{(-)})t} K_N(t). \quad (7')$$

$K_N(t)$  is given by (8). Here

$$V_N^{(-)*} \chi_N^{(-)} = U_N^* (W^*) \chi_N^{(-)};$$

$U_N(W)$  is defined by (10).

For scattering states of  $N$  particles equation (6') reads

$$(E_{\lambda(N)} - P_N H P_N - V_N^{(-)*}) \Phi_{\lambda(N)N}^{(-)} = 0, \quad (11')$$

and hence

$$\Phi_{\lambda(N)N}^{(-)} = |\lambda(N)\rangle + \frac{1}{E_{\lambda(N)} - P_N H P_N - V_N^{(-)*} - i\varepsilon} V_N^{(-)*} (E_{\lambda(N)}) |\lambda(N)\rangle. \quad (12')$$

Here

$$\Phi_{\lambda(N)N}^{(-)} = P_N \Phi_{\lambda(N)}^{(-)}. \quad (13')$$

We note that from the first equation (1) it follows that

$$P_{\perp N} \Phi_{\lambda(N)}^{(-)} = \frac{1}{E_{\lambda(N)} - P_{\perp N} H P_{\perp N} - i\varepsilon} P_{\perp N} H P_N \Phi_{\lambda(N)}^{(-)}, \quad (14')$$

if  $\Psi(t_0) = \Psi_N(t_0)$  and  $t_0 \rightarrow +\infty$ .



By means of a calculation similar to the previous calculations we obtain for the scattering amplitudes (16')

$$T_{\lambda(N_1)}^{(-)}(\lambda'(N_2)) = \langle \Phi_{\lambda'(N_2)N_2}^{(-)} V_{N_2N_1}^{(-)}(N_2, E_{\lambda(N_1)}) | \lambda(N_1) \rangle, \quad (17')$$

where

$$V_{N_2N_1}^{(-)}(N_2, E_{\lambda(N_1)}) = P_{N_2}(H - E_{\lambda(N_1)})P_{N_1} - i \int_0^\infty dt e^{i(P_{N_2}HP_{N_1} + V_{N_2N_1}^{(-)})t} K_{N_2N_1}(N_2, E_{\lambda(N_1)}, t); \quad (19')$$

$K_{N_2N_1}(N_2, E_{\lambda(N_1)}, t)$  is given *mutatis mutandis*, by (20). Here

$$V_{N_2N_1}^{(-)*}(N_2, E_{\lambda(N_1)})\chi_{N_1}^{(-)} = U_{N_2N_1}^*(N_2, E_{\lambda(N_1)}, W)\chi_{N_1}^{(-)}, \quad (21')$$

where  $U_{N_2N_1}(N_2, E_{\lambda(N_1)}, W)$  is defined *mutatis mutandis*, by (18). Further, we have

$$T_{\lambda(N_1)}^{(-)}(\lambda'(N_2)) = \langle \lambda'(N_2) | V_{N_2N_1}^{(-)}(N_2, E_{\lambda(N_1)}) | \lambda(N_1) \rangle + \\ + \langle \lambda'(N_2) | V_{N_1}^{(-)}(E_{\lambda'(N_2)}) \frac{1}{E_{\lambda'(N_2)} - P_{N_2}HP_{N_2} - \dot{V}_{N_2}^{(-)} + i\varepsilon} V_{N_2N_1}^{(-)}(N_2, E_{\lambda(N_1)}) | \lambda(N_1) \rangle \quad (23)$$

The approximation form of (23') is

$$T_{\lambda(N_1)}(\lambda'(N_2)) = \langle \lambda'(N_2) | V_{N_2N_1}^{(-)}(N_2, E_{\lambda(N_1)}) | \lambda(N_1) \rangle + \\ + \sum_{\lambda''(N_2)} \frac{T_{\lambda'(N_2)}^{(-)}(\lambda''(N_2)) T_{\lambda(N_1)}^{(-)}(\lambda''(N_1))}{E_{\lambda'(N_2)} - E_{\lambda''(N_2)} + i\varepsilon} + \\ + \sum_{b_{N_2}} \frac{\langle \chi_{N_2b_{N_2}}^{(-)} V_{N_2N_2}^{(-)}(N_2, E_{\lambda'(N_2)}) | \lambda'(N_2) \rangle * \langle \chi_{N_2b_{N_2}}^{(-)} V_{N_2N_1}^{(-)}(N_2, E_{\lambda(N_1)}) | \lambda(N_1) \rangle}{E_{\lambda'(N_2)} - \bar{E}_{b_{N_2}} + i\Gamma_{b_{N_2}} + i\varepsilon} \quad (25')$$

The first term on the r. h. s. above represents the Born approximation for the transition  $\lambda(N_1) \rightarrow \lambda'(N_2)$  with the exact „interaction” operator  $V_{N_2N_1}^{(-)}(N_2, E_{\lambda(N_1)})$  of  $N_2$  particles with  $N_1$  particles.

## КРАТКОЕ СОДЕРЖАНИЕ

Круликовски, Общие уравнение в теории поля для амплитуды рассеянных частиц.

В работе получены на основании поля точные соотношения для элементов матрицы S, отвечающих двоим заданным числам части. Все элементы с другим числом частиц элиминировались. Общее уравнение Лоу выведенное в предыдущей работе (Круликовски 1957) есть специальным случаем, в котором два различаемые числа частиц были идентичными. Если эти два числа частиц, предположим  $N_1$  и  $N_2$  с переходом  $N_1 \rightarrow N_2$ , н. пр. фотопродукция пионов с эффектом комптона на нуклонах. Если амплитуда перехода процесса  $N_1 \rightarrow N_2$  известна, тогда амплитуда процесса  $N_1 \rightarrow N_2$  выполняет линейное уравнение.

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# ESTIMATION OF THE HEIGHT OF THE POTENTIAL BARRIER OF HINDERED ROTATION IN THE $\text{CH}_3\text{SH}$ MOLECULE BY MEANS OF THERMAL NEUTRON SCATTERING

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In this paper the potential barrier height  $H$  of internal hindered rotations of methyl mercaptan molecules was estimated by means of a method based on the scattering of thermal neutrons with a Maxwellian energy distribution (mean neutron energy  $E = 0.037$  eV). The cross section of  $\text{CH}_3\text{SH}$  molecules measured by thermal neutron scattering was  $\sigma = (194.5 \pm 5)$  barns. This was determined by the method of relative attenuation of the beam. Water was used as a standard liquid ( $\sigma_{\text{H}_2\text{O}} = 91$  barns). The cross section for rigid  $\text{CH}_3\text{SH}$  molecules calculated on the basis of the theory of Sachs and Teller was  $\sigma_{\text{rig}} = 258$  barns.

Assuming a potential barrier height of  $H = 705$  cal/mol and taking into account the hindered rotation and the vibration of the atoms, the authors calculated the cross section of the  $\text{CH}_3\text{SH}$  molecules. The result obtained was  $\sigma_{\text{theor.}} = 202$  barns. The cross section for collisions that are elastic with regard to hindered rotation was also calculated under the assumption that  $H = 1460$  cal/mol, this value being obtained by thermodynamical methods. The discussion of the results leads to the conclusion that a height of 705 cal/mol found by microwave spectroscopic methods should be ascribed to the potential barrier in the methyl mercaptan molecule rather than the value obtained by thermodynamic methods.

## 1. Introduction

In 1953 and 1954 measurements were made by one of the authors (Janik 1953 and 1954) of the cross section for diffuse scattering of thermal neutrons by molecules of liquid  $\text{CH}_3\text{OH}$ . These measurements were carried out in order to investigate the influence of hindered rotation in  $\text{CH}_3\text{OH}$  molecules on neutron scattering and to check the theory of this effect as given by Kołos (1954 and 1955). The results obtained were within the limits of error, in agreement with this theory, it being assumed that the potential barrier height of the hindered rotation in the  $\text{CH}_3\text{OH}$  molecule had the value of 1110 cal/mol (Swalen 1955).

There exist important arguments, on the basis of which it may be supposed that the obtained agreement of experiment with theory was a chance occurrence. It is known that methyl alcohol is a strongly associated liquid, which, according to the theory of Sachs and Teller (1941), should cause an increase of the cross section for neutron scattering as compared to the case with no association. On the other hand, however, the discovered vibrations in liquid  $\text{CH}_3\text{OH}$  of frequency  $250 \text{ cm}^{-1}$ , and interpreted as vibrations of the hydrogen atom of the OH group perpendicular to the direction of the  $\text{O} - \text{H} \cdots \text{O}$  hydrogen bond, should produce a reduction of the cross section. The agreement obtained between the theoretical and experimental values of the cross section might be the result of a chance superposition of the two effects.

This view gave rise to the undertaking described in this paper — the measurement of the cross section of the  $\text{CH}_3\text{SH}$  molecules for thermal neutron scattering. Because of the weakness here of the  $\text{S} - \text{H} \cdots \text{S}$  hydrogen bond, the suggestion that the influence of the association is not taken into account loses its meaning.

It should also be noted that the methods commonly used thus far for determining the potential barrier height of hindered rotation does not in general lead to consistent results. Thus e. g. for mercaptan molecules, Kilb (1955), using the spectroscopic data, found the potential barrier  $H = 705 \text{ cal/mol}$ , while thermodynamic methods gave the result  $H = 1460 \text{ cal/mol}$ .

It might be expected that the results of the cross section measurements for neutron scattering in methyl mercaptan would allow the estimation of the potential barrier height and eventually decide between the values obtained by the methods cited above.

## 2. Theoretical Results

Because of the already mentioned divergence of results for the potential barrier height obtained by spectroscopic and thermodynamic methods, the cross section of the mercaptan molecules was calculated for both  $H = 705 \text{ cal/mol}$  and  $H = 1460 \text{ cal/mol}$ .

For both these values of the potential barrier the coefficients  $a_n$  of the Fourier expansion for the periodic part of the Mathieu functions describing the hindered rotation were calculated<sup>1</sup>

$$M_{\varrho m}(\varphi') = e^{-i\tau\beta_i\varphi'} \sum_{n=-\infty}^{\infty} a_n^{(\varrho_i\tau_i)} e^{in\varphi'} \quad (1)$$

From the formula

$$b_0(\tau_i, \tau_f) = \sum_{n=0}^{\infty} a_n(\varrho_i\tau_i) a_n(\varrho_f\tau_f) \quad (2)$$

<sup>1</sup> For the notation used in this paper cf. Kołos 1954, 1955.



the coefficients  $b_0^2$  were then calculated for various collisions taking place with a change of quantum number  $\tau$  (describing the rotation of the entire molecule about the axis of hindered rotation), but which are elastic with regard to the hindered rotation. Some values of these coefficients are given in the table below.

Table I

$\tau_i \leftrightarrow \tau_f$			$0 \leftrightarrow 1$	$0 \leftrightarrow 2$	$0 \leftrightarrow 3$	$0 \leftrightarrow 4$	$0 \leftrightarrow 5$	$0 \leftrightarrow 6$
$b_0^2$	$H = 705 \text{ cal/mol}$	$\text{CH}_3$	0.978	0.939	0.884	0.805	0.723	0.624
		$\text{SH}$	0.945	0.828	0.663	0.449	0.320	0.203
	$H = 1460 \text{ cal/mol}$	$\text{CH}_3$	0.991	0.996	0.93	0.87	0.81	0.745
		$\text{SH}$	0.971	0.885	0.77	0.63	0.49	0.360

The cross section of mercaptan molecules for collisions that are elastic with regard to hindered rotation was calculated from the formula (Kołos 1955)<sup>2</sup>

$$\sigma_{m_i} = \frac{4 \sigma_0 (\mu_0 \mu_1 \mu_2 \mu_3)^{1/2}}{I_{m_i}} \sum_{\tau_f} b_0^2(\tau_i, \tau_f) \sum_{n=0}^{\infty} \frac{(-1)^n D_n + \tau_{if}}{n! (2\tau_{if} + n)!} \quad (3)$$

where

$$D_n = \frac{(2n)! (s+n)! (8\mu' E_i a^2/\hbar^2)^n}{(n!)^2 (n+1)} \sum_{m=0}^{2p} \gamma_m \frac{(d+m+n)!}{(d+s+m+2n+1)!} \quad (4)$$

The results obtained in this manner, averaged over the initial states, are shown graphically in Fig. 1.

The vibrations of atoms in the molecule still have to be taken into account. Since the calculation of the influence of vibrations on the cross section would be very complicated in our case, we have assumed that it is the same percent as in the methane molecule (Messiah 1951).

In this way, for a neutron energy equal to 0.037 eV, which corresponds to the mean value of the energy of a Maxwell distribution at room temperature, the following values of the cross section of the mercaptan molecule were obtained

$$\sigma = 181 \times 10^{-24} \text{ cm}^2 \text{ for } H = 705 \text{ cal/mol}$$

$$\sigma = 195 \times 10^{-24} \text{ cm}^2 \text{ for } H = 1460 \text{ cal/mol}$$

However, calculations show that for  $H = 705 \text{ cal/mol}$  the first excited level of hindered rotation lies only  $150 \text{ cm}^{-1}$  above the ground state level. As a result the

<sup>2</sup> In the same formula derived in the paper cited, there is a misprint. The results listed there, however, were obtained by means of the correct formula whose form is given above.

neglecting of cross section due to collisions that are inelastic as regards hindered rotation is not justified.

By using formula (3) and calculating the coefficients  $b_0^2$  for the transitions connected with the first excitation of the hindered rotation it was found that for

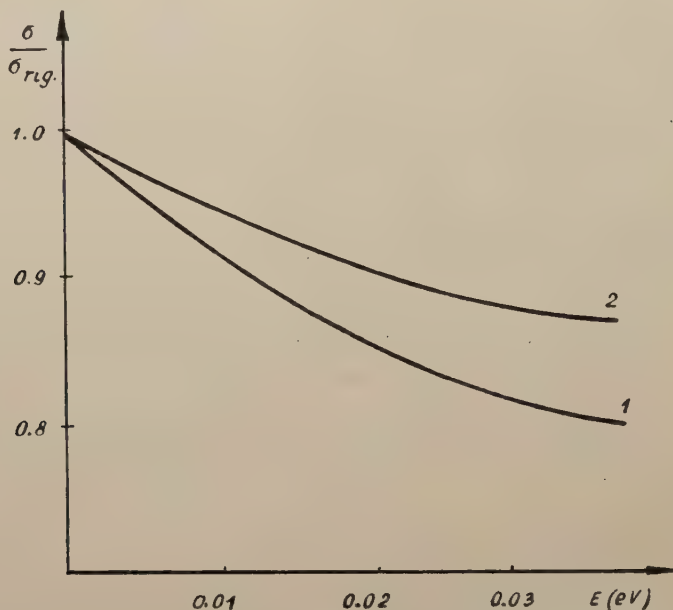


Fig. 1 Cross section of methyl mercaptan molecule as a function of the initial neutron energy calculated by taking into account the effect of rotation and internal hindered rotation. Curve 1 corresponds to a potential barrier height  $H = 705$  cal/mol, while curve 2 to a height  $H = 1469$  cal/mol.

$H = 705$  cal/mol the cross section corresponding to these collisions is equal to  $21 \times 10^{-24}$ . Hence the total cross section of the molecule for this potential barrier height is  $202 \times 10^{-24}$  cm<sup>2</sup>.

### 3. Experimental method

The equipment used for measuring the cross section for neutron scattering consists of a source of slow neutrons, a scatterer and a detecting arrangement.

The neutron source was 100 mg of radium mixed with beryllium. The neutrons were obtained by slowing down in paraffin shaped in the form of a „neutron gun”.

The scatterer ( $\text{CH}_3\text{SH}$ ) was placed in a flat-walled brass vessel whose walls were thick enough to withstand the vapour pressure at room temperature of the liquid under investigation. Because of the fact that the vessel was to be used for investigations of other substances with a saturated vapour pressure greater than methyl mercaptan, it was made to withstand a pressure of about 100 atmospheres. The brass walls bound-

ing the layer of the investigated substance had a thickness of 5 mm for this reason. The layer of the substance under investigation had a thickness of 5.3 mm.

A multi-plate ionization chamber containing a set of 6 electrodes covered with a layer of borium of thickness to about 3 mg/cm<sup>2</sup> and filled with argon to a pressure of about 0.5 atmospheres (Budzanowski and Grotowski 1956) was used as a slow-neutron detector.

The electronic equipment working with the chamber, and designed to detect electron pulses arising in the chamber, consisted of a pre-amplifier, a model 100 amplifier (according to Elmore), a Schmidt discriminator (Elmore), and a scaler.

Absolute cross section measurements for neutron scattering must be made in a suitable ideal geometry in which the scatterer is placed sufficiently far from the source and from the detector. However, because of the weak source of neutrons which was used in this work, it was decided to work with relatively small distances between the source, scatterer and detector; to make up for this, relative measurements were made by using water as a standard liquid with a known cross section. In this geometry a certain percent of scattered neutrons found their way to the detector. This fact caused a deviation from the exponential character of the absorption which was difficult to estimate if only absolute measurements were made.

With the use of relative methods of measurement, however, the matter looks as follows:

The number  $I_w$  of neutrons making their way to the detector, with water used as the scattering substance, is expressed by the formula

$$J_w = J_0 e^{-\sigma_w n_w x} + J_1 (1 - e^{-\sigma_w n_w x}) \quad (5)$$

where  $I_0$  is the intensity of the beam of neutrons falling on the detector,  $\sigma_w$  is the cross section of the water molecules for neutron scattering,  $n_w$  is the number of molecules of water in 1 cm<sup>3</sup>,  $x$  is the thickness of the scatterer, while  $I_1$  is a factor which is determined from the water measurement and whose value can then be inserted into a similar equation written for the scattering liquid under investigation.<sup>1</sup> Using methyl mercaptan as a scattering liquid, we obtain the above formula in the following form

$$J_m = J_0 e^{-\sigma_m n_m x} + J_1 (1 - e^{-\sigma_m n_m x}) \quad (6)$$

Eliminating  $I_1$  from both equations we obtain

$$\sigma_m = \frac{1}{n_m \cdot x \cdot \log e} \log \frac{J_0 - \frac{J_w - J_0 e^{-\sigma_w n_w x}}{1 - e^{-\sigma_w n_w x}}}{J_n - \frac{J_w - J_0 e^{-\sigma_w n_w x}}{1 - e^{-\sigma_w n_w x}}} \quad (7)$$

<sup>1</sup> The factor  $I_1$  is defined as the percent of scattered neutrons which, because of imperfect geometry, enter the detector.

From this formula the cross section is calculated after inserting the experimentally measured values  $x$ ,  $I_0$ ,  $I_w$ , and  $I_m$ . From the discussion of the errors it follows that the errors of the measurement of  $x$  and  $I_0$  influence the value of the error of  $\sigma_w$  to a very small degree, so that the main part of the time of the measurement was devoted to the measuring of the values  $I_w$  and  $I_m$ .

The positions of the source, scatterer, and detector in the geometry used for the measurements are shown in Fig. 2.

In order to eliminate any eventual changes with time in the threshold of the equipment, the measurements were made by using two identical absorption vessels,

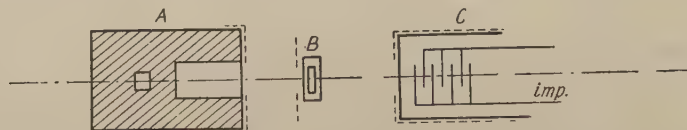


Fig. 2. — Geometry in which the measurements were made: a) neutron gun, b) vessel with the scattering liquid under investigation, c) 6-plate ionization chamber, d) cadmium shielding against scattered neutrons.

one of which was filled with water, while the second with mercaptan; the vessels were measured alternately over fifteen minute periods. At regular intervals measurements were made of  $I_0$  by spilling out the water and using an empty vessel.

The identicalness of both absorption vessels was also investigated by placing them (filled with water) alternately for a number of 15 minute periods in the same positions as for the main measurements. It was established that the vessels are not completely identical and that the number of counts obtained by using the second one when compared with the number of counts obtained by using the first had to be multiplied by a factor of 0.983.

In order to calculate  $n_w$  it was necessary to know the density of mercaptan at the temperature during the measurement, that is, at a temperature of 20°C. The measurement of this density was made on the basis of the values of the density at 0°C as found in the tables. This measurement was made as follows: a column of mercaptan of a certain height was closed in a thermometric capillary tube. Next the variation of the height of the column with temperature was investigated. Because of the considerable distance from the critical temperature, it was possible to neglect the density of the vapour. If the value of the density at a temperature of 0°C is known, it is possible to calculate from these measurements the value of the density at 20°C. This value was 0.86 g/cm<sup>3</sup>.

#### 4. Method of preparing the CH<sub>3</sub>SH

Methyl mercaptan was obtained by the method described by Arndt (1921). Obtaining CH<sub>3</sub>SH by this method entails two steps: First, from a suitable quantity of dimethyl sulphate, thiourea, and water there is obtained an intermediary product



having the formula  $(C_2H_4N_2S)_2H_2SO_4$ . Then, after boiling this product in a solution of NaOH, methyl mercaptan is obtained. The methyl mercaptan is passed through a bath of  $H_2SO_4$  and a tube with  $CaCl_2$ .

Details concerning the quantity of substance, the procedure, and so on are contained in the above-mentioned paper.

Condensation of the  $CH_3SH$  obtained takes place in a spiral glass tube connected to the vessel used to collect the  $CH_3SH$  that has been formed. The tube is immersed in finely divided solid  $CO_2$ .

### 5. Results of the Measurements and Discussion

The cross section obtained in the measurements for the scattering of thermal neutrons by liquid methyl mercaptan molecules is

$$\sigma_M = (194.5 \pm 5) \times 10^{-24} \text{ cm}^2,$$

while the theoretical value of the cross section for the hindered rotation barrier height potential  $H = 705$  cal/mol as given in Section 2 is  $\sigma = 202 \times 10^{-24} \text{ cm}^2$ .

It should be remembered, however, that the formula (3) was derived for the assumption that the energy changes connected with the excitation of the molecule are small in comparison to the energy of the incident neutrons. However, since the excitation of hindered rotation is always connected with the excitation of rotation of the entire molecule, then in the case of inelastic collisions (as regards hindered rotations) the above-mentioned assumption is not satisfied so well. The theoretical result listed  $\sigma = 202 \times 10^{-24} \text{ cm}^2$  may therefore contain an error. This error would be still greater if the barrier height was  $H = 1460$  cal/mol, since then the first excited level of hindered rotation would lie about  $210 \text{ cm}^{-1}$  above the ground state. Without performing the calculations, it can be stated, however, that by taking  $H = 1460$  cal/mol we would obtain a cross section for mercaptan greater than in the case of  $H = 705$  cal/mol, i. e. greater than  $202 \times 10^{-24} \text{ cm}^2$ .

The error which we commit by using formula (3) for inelastic collisions cannot really be estimated; it is known however, that it leads to a too great theoretical value for the cross section. This follows from the fact that by using the formula we take into account also such inelastic (with regard to rotation of the entire molecule) collisions which violate the principle of the conservation of energy.

It therefore seems that the experimentally obtained value for the cross section indicates a height of the potential barrier for hindered rotation  $H = 705$  cal/mol rather than the height  $H = 1460$  cal/mol found by thermodynamic methods.

A far more certain conclusion regarding the height of this barrier could be obtained by using a neutron velocity selector. Then, by measuring the cross section as function of the neutron energy, the energies for exciting hindered rotation could be determined directly; an increase in the cross section should then be expected for

these energies. On the other hand, knowing these energies, we could calculate the hindered rotation potential barrier height without knowing the value of the cross section. This would eliminate the effect of the approximations used in the theory of scattering.

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#### КРАТКОЕ СОДЕРЖАНИЕ

А. Будзановский, К. Гротовский, Я. Яник, В. Колос, Ф. Манявский, Г. Ржаны, А. Шкатула, А. Ваниц. Оценка высоты потенциального барьера заторможенной ротации в частице  $\text{CH}_3\text{SH}$  при помощи эффекта рассеяния медленных нейтронов.

В настоящей работе расценена высота потенциального барьера  $V_0$  внутренней заторможенной ротации частицы метилового меркаптана  $\text{CH}_3\text{SH}$ , пользуясь методом рассеяния медленных нейтронов с максвелловским разложением (средняя энергия нейтронов  $E_n = 0,037$  eV). Измерено эффективное сечение рассеяния медленных нейтронов частицы  $\text{CH}_3\text{SH}$   $\sigma = (194,5 \pm 5)$  барнов. Определено оно методом относительно ослабления связки. Как эталонная жидкость взята вода ( $\sigma_{H_2O} = 91$  барнов). Эффективное сечение жесткой частицы  $\text{CH}_3\text{SH}$  вычислено на основании теории Сахса и Теллера  $\sigma_{\text{rig}} = 258$  барнов.

Допуская высоту потенциального барьера  $V_0 = 705$  cal/mal и принимая во внимание заторможенную ротацию, а также вибрацию атомов, вычислено эффективное сечение молекулы  $\text{CH}_3\text{SH}$ , получая  $\sigma_{\text{теор}} = 202$  барнов. Учитывая заторможенную ротацию, вычислено тоже, допуская  $V_0 = 1460$  cal/mal, эффективное сечение электрических столкновений. Обсуждение результатов приводит к заключению, что потенциальному барьеру молекулы метилового меркаптана скорее следует приписать высоту  $V_0 = 750$  cal/mal, найденную методом микроволновой спектроскопии, чем  $V_0 = 1460$  cal/mal, т. е. величину, полученную термодинамическими методами.

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# THE APPLICATION OF THE TIGHT BINDING METHOD TO THE INVESTIGATION OF ENERGY BANDS IN HEXAGONAL CLOSE-PACKED STRUCTURE. I.

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Tables for reduction of the matrix components of energy in the tight binding method have been prepared for hexagonal close-packed lattices.

The tight binding or LCAO method originally proposed by Bloch (1928) can be applied satisfactorily to the investigation of the symmetry properties of energy bands in crystals. Slater and Koster (1954) worked out this method in detail, discussed the possible approximations and the validity of the application of this method to real cases.

A rigorous application of this method is hardly possible on account of the enormous amount of numerical work. Taking into account the approximations discussed by Slater and Koster, this method can be applied to crystals, in which the electrons are tightly bound. The LCAO method can be applied also in the case, when the electrons are not tightly bound, but then only as an interpolation method. The energy integrals are then not computed analytically but they are used as disposable constants which can be found using the energy values calculated by other methods at restricted symmetry points in the Brillouin zone.

The calculations of Slater and Koster have been performed for simple cubic structures, namely for a simple cubic lattice; for face- and body-centered cubic lattices and for a cubic structure with basis, in particular for the diamond lattice.

In the present work the LCAO method is used to investigate the properties of energy bands in hexagonal close-packed structure. The calculations for hexagonal close-packed structure are more laborious because the unit cell has two non-equivalent atoms and the geometry of this lattice is more complicated, the directions along the axes of rectangular co-ordinate system being non-equivalent.

There are in literature a few papers on energy bands in hexagonal structure. Herring and Hill (1940) have applied to beryllium the method of orthogonalized

plane waves. Schiff (1955) investigated the symmetry properties of energy bands in titanium by the cellular method.

The metal to which the LCAO method could be applied is the hexagonal form of cobalt;  $\alpha$  — Co. Cobalt belongs to the group of transition elements, as Ni and Fe, the  $d$  states of which can be treated with the tight binding approximation. For instance Fletcher and Wohlfarth (1951) and Fletcher (1952) investigated with the help of this method the energy bands in face-centered Ni. Suffczyński (1956) calculated two-center integrals for body-centered Fe.

The hexagonal close-packed lattice can be described as a simple hexagonal lattice with two non-equivalent atoms in the unit cell. The primitive translation vectors in rectangular co-ordinate system are:  $\mathbf{A}_1 = (a/2, -\sqrt{3}a/2, 0)$ ,  $\mathbf{A}_2 = (a/2, \sqrt{3}a/2, 0)$ ,  $\mathbf{A}_3 = (0, 0, c)$ , where  $a$  is lattice constant in the horizontal plane. The basis vectors are:  $\mathbf{t}_1 = (0, 0, 0)$ ,  $\mathbf{t}_2 = (a/2, \sqrt{3}a/6, c/2)$ , when the origin of the co-ordinate system coincide with the position of an atom of the lattice. The simple lattice with an atom at  $(0, 0, 0)$  is denoted by the index 1, and the lattice with an atom at  $(a/2, \sqrt{3}a/6, c/2)$  by the index 2.

For convenience we use different length units along different axes of the rectangular co-ordinate system, namely  $\alpha = a/2$ ,  $\beta = \sqrt{3}a/2$ ,  $\gamma = c/2$  in the  $x$ ,  $y$ ,  $z$  directions respectively.

In our calculations we use the model of the hexagonal ideal close-packed lattice, i. e., we put the distance between two nearest non-equivalent atoms equal to  $a$ ;

$|\mathbf{t}_2| = a$ . Then  $c/a = \sqrt{\frac{8}{3}} = 1.63$ . This is approximately fulfilled for many crystals with hexagonal structure, for instance for  $\alpha$  — Co we have  $c/a = 1.62$ .

The energy dependence on the wave vector  $\mathbf{k}$  will be obtained by solving the secular equation

$$\det | (m/n)_{\omega\omega'} - \delta_{mn} \delta_{\omega\omega'} E | = 0,$$

where  $(m/n)_{\omega\omega'}$  are the matrix components of the Hamiltonian (energy) between corresponding Bloch sums. In the present work these components are computed using firstly the general three-center integrals and subsequently the two-center integrals.

The general formula for the matrix components of energy is given by

$$(m/n)_{\omega\omega'} = \exp [i\mathbf{k}(\mathbf{t}_\omega - \mathbf{t}_{\omega'})] \sum_l \exp (i\mathbf{k}\mathbf{r}_l) \int \varphi_m^*(\mathbf{r} - \mathbf{t}_{\omega'}) H \varphi_n(\mathbf{r} - \mathbf{r}_l - \mathbf{t}_\omega) d\mathbf{r}.$$

$m, n$  denote here atomic states,  $\varphi_n$  are the atomic functions,  $\mathbf{r}_l = l_1 \mathbf{A}_1 + l_2 \mathbf{A}_2 + l_3 \mathbf{A}_3$  — translation vectors ( $l_1, l_2, l_3$  are integers),  $\mathbf{t}_\omega$  — basis vectors. The Hamiltonian  $H = -\Delta + V(\mathbf{r})$  is an Hermitian operator.  $V(\mathbf{r}) = \sum_l [U(\mathbf{r} - \mathbf{r}_l) + U(\mathbf{r} - \mathbf{r}_l - \mathbf{t}_2)]$  is the periodic potential of the whole crystal, thus  $V(\mathbf{r} + \mathbf{r}_l) = V(\mathbf{r})$ .  $U(\mathbf{r} - \mathbf{r}_l)$  is the potential of an isolated ion located at the point  $\mathbf{r}_l$ . The energy integrals ( $E$ -integrals)



have the form

$$E_{m,n}(\mathbf{t}_w, \mathbf{r}_l + \mathbf{t}_w) = \int \varphi_m^*(\mathbf{r} - \mathbf{t}_w) H \varphi_n(\mathbf{r} - \mathbf{r}_l - \mathbf{t}_w) d\mathbf{r}.$$

The matrix components are calculated for the following states:  $s$ ,  $p$  (3 functions of the type  $x$ ,  $y$ ,  $z$  times  $f_1(r)$ , denoted by  $p_j$ ),  $d$  (5 functions of the type  $xy$ ,  $yz$ ,  $xz$ ,  $x^2 - y^2$ ,  $3z^2 - r^2$  times  $f_2(r)$ , denoted by  $d_q$ ). Since we have nine such states and a unit cell contains two non-equivalent atoms, we construct 18 Bloch sums. The general matrix of energy has  $18 \times 18 = 324$  components.

Using symmetry properties of the Hamiltonian and of atomic functions we can perform the reduction of these matrix components. It is convenient at this moment to put the origin of the co-ordinate system in the middle point of the line joining two non-equivalent atoms in the unit cell. In such a system the basis vectors are  $\mathbf{t}'_1$  and  $\mathbf{t}'_2 = -\mathbf{t}'_1 = \frac{1}{2} \mathbf{t}_2$ .

The periodic potential takes the form

$$V(\mathbf{r}) = \sum_l \left[ U \left( \mathbf{r} - \mathbf{r}_l - \frac{1}{2} \mathbf{t}_2 \right) + U \left( \mathbf{r} - \mathbf{r}_l + \frac{1}{2} \mathbf{t}_2 \right) \right] \quad \text{and} \quad \text{therefore}$$

$V(\mathbf{r}) = V(-\mathbf{r})$ . We also use the fact, that to every vector  $\mathbf{r}_l$  corresponds the vector  $\mathbf{r}'_l = -\mathbf{r}_l$ .

We notice the following general relation

$$(m/n)_{w'\omega} = [(n/m)_{w\omega}]^*$$

Further relations are given in Table I.

TABLE I

$(s/s)_{11} = (s/s)_{22}$	$(s/s)_{12} = (s/s)_{21}^*$
$(s/p_j)_{11} = -(s/p_j)_{22}^*$	$(s/p_j)_{12} = -(s/p_i)_{21}^*$
$(s/d_q)_{11} = (s/d_q)_{22}^*$	$(s/d_q)_{12} = (s/d_q)_{21}^*$
$(p_j/p_j)_{11} = (p_j/p_j)_{22}$	$(p_j/p_j)_{12} = (p_j/p_j)_{21}^*$
$(p_j/p_i)_{11} = (p_j/p_i)_{22}$	$(p_j/p_i)_{12} = (p_j/p_i)_{21}^* \quad i \neq j$
$(p_j/d_q)_{11} = -(p_j/d_q)_{22}^*$	$(p_j/d_q)_{12} = -(p_j/d_q)_{21}^*$
$(d_q/d_q)_{11} = (d_q/d_q)_{22}$	$(d_q/d_q)_{12} = (d_q/d_q)_{21}^*$
$(d_q/d_r)_{11} = (d_q/d_r)_{22}^*$	$(d_q/d_r)_{12} = (d_q/d_r)_{21}^* \quad q \neq r$

From the total of 324 components only 90 components must now be considered: 45 components of the type

$$(m/n)_{11} = \sum_l \exp(i\mathbf{k}\mathbf{r}_l) \int \varphi_m^*(\mathbf{r}) H \varphi_n(\mathbf{r} - \mathbf{r}_l) d\mathbf{r}$$

and 45 components of the type

$$(m/n)_{12} = \sum \exp[i\mathbf{k}(\mathbf{r}_l + \mathbf{t}_2)] \int \varphi_m^*(\mathbf{r}) H \varphi_n(\mathbf{r} - \mathbf{r}_l - \mathbf{t}_2) d\mathbf{r}.$$

In the above integrals the origin of the co-ordinate system is again located at the position of an atom. This system will be used exclusively in the following.

We make now the nearest-neighbours approximation. Every atom in a hexagonal ideal close-packed lattice has 12 nearest neighbours: six neighbours in lattice 1 and six in lattice 2. Therefore, in the matrix components  $\langle m/n_{11} \rangle$  there remain only seven  $E$ -integrals corresponding to the lattice sites  $\mathbf{r}_1$  (0, 0, 0); (1, -1, 0), (2, 0, 0), (1, 1, 0), (-1, -1, 0), (-2, 0, 0), (-1, 1, 0) in terms of  $\alpha$ ,  $\beta$ ,  $\gamma$  and in  $\langle m/n \rangle_{12}$  six  $E$ -integrals corresponding to  $\mathbf{r}_1 + \mathbf{t}_2$ : (1, 1/3, 1), (-1, 1/3, 1), (0, -2/3, 1), (1, 1/3, -1), (0, -2/3, -1). So  $7 \times 45 + 6 \times 45 = 585$   $E$ -integrals remain to be calculated. Not all of them are independent. The reduction of these integrals must be performed. Here we use more particular symmetries of the Hamiltonian and atomic functions. We perform the orthogonal transformations which carry the hexagonal close-packed lattice into itself. Under these symmetry transformations the Hamiltonian is invariant.

We take into account the following transformations: 1) reflections in three vertical planes, the normals to which make the angles  $\frac{2}{3} \pi$  among themselves; one of these planes is the plane  $x = 0$ , 2) reflection in the horizontal plane  $z = 0$ . From these transformations we can obtain all other necessary transformations.

Under these transformations the atomic functions transform in some definite way. If we take for instance one of the  $d$  functions located on the atom  $\mathbf{r}_l$ , then after any one of the above transformations we obtain a linear combination of the  $d$  functions all located on some other atom, say  $\mathbf{r}_k$ .

In the first step of the reduction of  $E$ -integrals we use only these symmetry transformations after which in a given matrix component, say  $\langle m_0/n_0 \rangle$ , only  $E$ -integrals remain with the same index  $m_0$  and  $n_0$ . By this treatment the non-vanishing matrix components can be divided into ten sets. Every set has different relations between the  $E$ -integrals. Therefore the  $\mathbf{k}$  dependence of all components in one set is the same.

First we write down all the components which belong to every set, secondly the relations between  $E$ -integrals in this set and lastly the  $\mathbf{k}$  dependence. We use here the following abbreviations:  $\xi = \alpha k_x = ak_x/2$ ,  $\eta = \beta k_y = \sqrt{3} a k_y/2$ ,  $\zeta = \gamma k_z = ck_z/2 = ak_z \sqrt{2/3}$ .

$$1. \langle s/s \rangle_{11}, \langle s/3z^2 - r^2 \rangle_{11}, \langle z/z \rangle_{11}, \langle 3z^2 - r^2/3z^2 - r^2 \rangle_{11}$$

$$E_{m,n}(0, 0, 0) \neq 0$$

$E_{m,n}(\mathbf{r}_1)$  — identical for six vectors  $\mathbf{r}_1$  corresponding to nearest neighbours in lattice 1.

$$\langle m/n \rangle_{11} = E_{m,n}(0, 0, 0) + 2E_{m,n}(2, 0, 0)(2 \cos \xi \cos \eta + \cos 2 \xi)$$

$$2. \langle s/s \rangle_{12}, \langle s/3z^2 - r^2 \rangle_{12}, \langle z/z \rangle_{12}, \langle 3z^2 - r^2/3z^2 - r^2 \rangle_{12}$$

$E_{m,n}(\mathbf{r}_1 + \mathbf{t}_2)$  — identical for six vectors  $(\mathbf{r}_1 + \mathbf{t}_2)$  corresponding to nearest neighbours in lattice 2.

$$(m/n)_{12} = 2E_{m,n} \left( 0, -\frac{2}{3}, 1 \right) \cos \xi \left[ \left( 2 \cos \xi \cos \frac{1}{3} \eta - \sin \frac{2}{3} \eta \right) + \right. \\ \left. + i \left( 2 \cos \xi \sin \frac{1}{3} \eta - \sin \frac{2}{3} \eta \right) \right]$$

$$3. (s/x)_{11}, (s/xy)_{11}, (x/y)_{11}, (x/x^2 - y^2)_{11}, (x/3z^2 - r^2)_{11}$$

$$(y/xy)_{11}, (z/xz)_{11}, (xy/x^2 - y^2)_{11}, (xy/z^2 - r^2)_{11}, (yx/xz)_{11}$$

$$E_{m,n}(0, 0, 0) = 0$$

$$E_{m,n}(1, -1, 0) = -E_{m,n}(-1, -1, 0)$$

$$E_{m,n}(1, 1, 0) = -E_{m,n}(-1, 1, 0)$$

$$E_{m,n}(2, 0, 0) = -E_{m,n}(-2, 0, 0)$$

$$(m/n)_{11} = 2 [E_{m,n}(1, -1, 0) - E_{m,n}(1, 1, 0)] \sin \xi \sin \eta + 2i \{ [E_{m,n}(1, -1, 0) + \\ + E_{m,n}(1, 1, 0)] \sin \xi \cos \eta + E_{m,n}(2, 0, 0) \sin 2\xi \}$$

$$4. (s/x)_{12}, (s/xy)_{12}, (x/y)_{12}, (x/x^2 - y^2)_{12}, (x/3z^2 - r^2)_{12}, (y/xy)_{12}, (z/xz)_{12}, (xy/x^2 - y^2)_{12},$$

$$(xy/3z^2 - r^2)_{12}, (yz/xz)_{12}$$

$$E_{m,n} \left( 1, \frac{1}{3}, 1 \right) = E_{m,n} \left( 1, \frac{1}{3}, -1 \right) = -E_{m,n} \left( -1, \frac{1}{3}, 1 \right)$$

$$= -E_{m,n} \left( -1, \frac{1}{3}, -1 \right)$$

$$E_{m,n} \left( 0, -\frac{2}{3}, 1 \right) = E_{m,n} \left( 0, -\frac{2}{3}, -1 \right) = 0$$

$$(m/n)_{12} = -4 E_{m,n} \left( 1, \frac{1}{3}, 1 \right) \sin \xi \cos \xi \left( \sin \frac{1}{3} \eta - i \cos \frac{1}{3} \eta \right)$$

$$5. (s/y)_{11}, (s/x^2 - y^2)_{11}, (x/xy)_{11}, (y/x^2 - y^2)_{11}, (y/3z^2 - r^2)_{11}, (z/yz)_{11}, (x^2 - y^2/3z^2 - r^2)_{11},$$

$$E_{m,n}(0, 0, 0) \neq 0$$

$$E_{m,n}(1, -1, 0) = E_{m,n}(-1, -1, 0)$$

$$E_{m,n}(1, 1, 0) = E_{m,n}(-1, 1, 0)$$

$$E_{m,n}(2, 0, 0) = E_{m,n}(-2, 0, 0)$$

$$(m/n)_{11} = E_{m,n}(0, 0, 0) + 2 [E_{m,n}(1, -1, 0) + E_{m,n}(1, 1, 0)] \cos \xi \cos \eta + \\ + 2E_{m,n}(2, 0, 0) \cos 2\xi + 2i [E_{m,n}(1, 1, 0) - E_{m,n}(1, -1, 0)] \cos \xi \sin \eta$$

$$6. (s/y)_{12}, (s/x^2 - y^2)_{12}, (x/x)_{12}, (y/y)_{12}, (x/xy)^6_{12}, (y/x^2 - y^2)_{12}, (y/3z^2 - r^2)_{12},$$

$$(z/yz)_{12}, (xy/xy)_{12}, (xz/xz)_{12}, (yz/yz)_{12}, (x^2 - y^2/x^2 - y^2)_{12}, (x^2 - y^2/3z^2 - r^2)_{12}$$

$$\begin{aligned}
 E_{m,n} \left( 1, \frac{1}{3}, 1 \right) &= E_{m,n} \left( 1, \frac{1}{3}, -1 \right) = E_{m,n} \left( -1, \frac{1}{3}, 1 \right) = E_{m,n} \left( -1, \frac{1}{3}, -1 \right) \\
 E_{m,n} \left( 0, -\frac{2}{3}, 1 \right) &= E_{m,n} \left( 0, -\frac{2}{3}, -1 \right) \\
 (m/n)_{12} &= 2 \cos \zeta \left[ 2 E_{m,n} \left( 1, \frac{1}{3}, 1 \right) \cos \xi \cos \frac{1}{3} \eta + E_{m,n} \left( 0, -\frac{2}{3}, 1 \right) \cos \frac{2}{3} \eta \right] + \\
 &+ 2i \cos \zeta \left[ 2 E_{m,n} \left( 1, \frac{1}{3}, 1 \right) \cos \xi \sin \frac{1}{3} \eta - E_{m,n} \left( 0, -\frac{2}{3}, 1 \right) \sin \frac{2}{3} \eta \right]
 \end{aligned}$$

7.  $(s/z)_{12}, (z/3z^2 - r^2)_{12}$

$$\begin{aligned}
 E_{m,n} \left( 1, \frac{1}{3}, 1 \right) &= E_{m,n} \left( -1, \frac{1}{3}, 1 \right) = E_{m,n} \left( 0, -\frac{2}{3}, 1 \right) \\
 &= -E_{m,n} \left( 1, \frac{1}{3}, -1 \right) = -E_{m,n} \left( -1, \frac{1}{3}, -1 \right) = -E_{m,n} \left( 0, -\frac{2}{3}, -1 \right) \\
 (m/n)_{12} &= -2 E_{m,n} \left( 1, \frac{1}{3}, 1 \right) \sin \zeta \left[ \left( 2 \cos \xi \sin \frac{1}{3} \eta - \sin \frac{2}{3} \eta \right) - \right. \\
 &\left. - i \left( 2 \cos \xi \cos \frac{1}{3} \eta + \cos \frac{2}{3} \eta \right) \right]
 \end{aligned}$$

8.  $(s/xz)_{12}, (z/z)_{12}, (y/xz)_{12}, (x/yz)_{12}, (z/xy)_{12}, (xy/yz)_{12}, (xz/x^2 - y^2)_{12}, (xz/3z^2 - r^2)_{12}$

$$\begin{aligned}
 E_{m,n} \left( 1, \frac{1}{3}, 1 \right) &= -E_{m,n} \left( 1, \frac{1}{3}, -1 \right) = -E_{m,n} \left( -1, \frac{1}{3}, 1 \right) \\
 &= E_{m,n} \left( -1, \frac{1}{3}, -1 \right) \\
 E_{m,n} \left( 0, -\frac{2}{3}, 1 \right) &= E_{m,n} \left( 0, -\frac{2}{3}, -1 \right) = 0 \\
 (m/n)_{12} &= -4 E_{m,n} \left( 1, \frac{1}{3}, 1 \right) \sin \xi \sin \zeta \left( \cos \frac{1}{3} \eta + i \sin \frac{1}{3} \eta \right)
 \end{aligned}$$

9.  $(s/yz)_{12}, (y/z)_{12}, (x/xz)_{12}, (y/yz)_{12}, (z/x^2 - y^2)_{12}, (xy/xz)_{12}, (yz/x^2 - y^2)_{12}, (yz/3z^2 - r^2)_{12}$

$$\begin{aligned}
 E_{m,n} \left( 1, \frac{1}{3}, 1 \right) &= -E_{m,n} \left( 1, \frac{1}{3}, -1 \right) = E_{m,n} \left( -1, \frac{1}{3}, 1 \right) \\
 &= -E_{m,n} \left( -1, \frac{1}{3}, -1 \right) \\
 E_{m,n} \left( 0, -\frac{2}{3}, 1 \right) &= -E_{m,n} \left( 0, -\frac{2}{3}, -1 \right)
 \end{aligned}$$



$$\begin{aligned}
(m/n)_{12} = & 2 \sin \zeta \left[ -2 E_{m,n} \left( 1, \frac{1}{3}, 1 \right) \cos \xi \sin \frac{1}{3} \eta + \right. \\
& + E_{m,n} \left( 0, -\frac{2}{3}, 1 \right) \sin \frac{2}{3} \eta \left. \right] + 2 i \sin \zeta \left[ 2 E_{m,n} \left( 1, \frac{1}{3}, 1 \right) \cos \xi \cos \frac{1}{3} \eta \right. \\
& + E_{m,n} \left( 0, -\frac{2}{3}, 1 \right) \cos \frac{2}{3} \eta \left. \right]
\end{aligned}$$

$$10. (x/x)_{11}, (y/y)_{11}, (xy/xy)_{11}, (xz/xz)_{11}, (yz/yz)_{11}, (x^2 - y^2/x^2 - y^2)_{11}$$

$$E_{m,n}(1, -1, 0) = E_{m,n}(-1, -1, 0) = E_{m,n}(-1, 1, 0) = E_{m,n}(1, 1, 0)$$

$$E_{m,n}(2, 0, 0) = E_{m,n}(-2, 0, 0)$$

$$(m/n)_{11} = E_{m,n}(0, 0, 0) + 4E_{m,n}(1, -1, 0) \cos \xi \cos \eta + 2E_{m,n}(2, 0, 0) \cos 2\xi$$

$E$ -integrals for remaining matrix components vanish for all  $\mathbf{r}_l$ , therefore these matrix components disappear:

$$\begin{aligned}
(s/z)_{11} &= (s/xz)_{11} = (s/yz)_{11} = (x/z)_{11} = (y/z)_{11} = (x/xz)_{11} \\
&= (x/yz)_{11} = (y/xz)_{11} = (y/yz)_{11} = (z/xy)_{11} = (z/x^2 - y^2)_{11} = (z/3z^2 - r^2)_{11} \\
&= (xy/xz)_{11} = (xy/yz)_{11} = (xz/x^2 - y^2)_{11} = (xz/3z^2 - r^2)_{11} \\
&= (yz/x^2 - y^2)_{11} = (yz/3z^2 - r^2)_{11} = 0.
\end{aligned}$$

Now among all the non-vanishing  $E$ -integrals only  $E$ -integrals for  $\mathbf{r}_l = \mathbf{R} = (2, 0, 0)$  and  $\mathbf{r}_l + \mathbf{t}_2 = \mathbf{T} = (0, -2/3, 1)$  are independent. Therefore, in the second step of the reduction, we express all integrals  $E_{m,n}(1, -1, 0)$  and  $E_{m,n}(1, 1, 0)$  in terms of  $E_{m,n}(\mathbf{R})$  and the integrals  $E_{m,n}(1, 1/3, 1)$  in terms of  $E_{m,n}(\mathbf{T})$ . Here we use the symmetry transformations, which were not taken into account previously. The component  $(m_0/n_0)$  will now contain the integrals with  $m$  and  $n$  not necessarily equal to  $m_0$  and  $n_0$ . We have only 71 independent  $E$ -integrals. The expressions for the remaining integrals are given in Table II.

TABLE II

$$\begin{aligned}
E_{s,x}(1, \pm 1, 0) &= \frac{1}{2} [E_{s,x}(\mathbf{R}) \pm \sqrt{3} E_{s,y}(\mathbf{R})] \\
E_{s,x} \left( 1, \frac{1}{3}, 1 \right) &= \sqrt{3} E_{s,y} \left( 1, \frac{1}{3}, 1 \right) = -\frac{1}{2} \sqrt{3} E_{s,y}(\mathbf{T}) \\
E_{s,y}(1, \pm 1, 0) &= \frac{1}{2} [\pm \sqrt{3} E_{s,x}(\mathbf{R}) - E_{s,y}(\mathbf{R})] \\
E_{s,xy}(1, \pm 1, 0) &= \frac{1}{2} [\pm \sqrt{3} E_{s,x^2-y^2}(\mathbf{R}) + E_{s,xy}(\mathbf{R})]
\end{aligned}$$

$$E_{s,xy} \left( 1, \frac{1}{3}, 1 \right) = \sqrt{3} E_{s,x^2-y^2} \left( 1, \frac{1}{3}, 1 \right) = -\frac{1}{2} \sqrt{3} E_{s,x^2-y^2} (T)$$

$$E_{s,xz} \left( 1, \frac{1}{3}, 1 \right) = \sqrt{3} E_{s,yz} \left( 1, \frac{1}{3}, 1 \right) = -\frac{1}{2} \sqrt{3} E_{s,yz} (T)$$

$$E_{s,x^2-y^2} (1, \pm 1, 0) = \frac{1}{2} [-E_{s,x^2-y^2} (R) \pm \sqrt{3} E_{s,xy} (R)]$$

$$E_{x,x} (1, -1, 0) = \frac{1}{4} [E_{x,x} (R) + 3 E_{y,y} (R)]$$

$$E_{x,x} \left( 1, \frac{1}{3}, 1 \right) = \frac{1}{4} [E_{x,x} (T) + 3 E_{y,y} (T)]$$

$$E_{y,y} (1, -1, 0) = \frac{1}{4} [3 E_{x,x} (R) + E_{y,y} (R)]$$

$$E_{y,y} \left( 1, \frac{1}{3}, 1 \right) = \frac{1}{4} [3 E_{x,x} (T) + E_{y,y} (T)]$$

$$E_{x,y} (1, \pm 1, 0) = \pm \frac{1}{4} \sqrt{3} E_{x,x} (R) - E_{x,y} (R) \mp \frac{1}{4} \sqrt{3} E_{y,y} (R)$$

$$E_{x,y} \left( 1, \frac{1}{3}, 1 \right) = \frac{1}{4} \sqrt{3} [-E_{x,x} (T) + E_{y,y} (T)]$$

$$E_{x,z} \left( 1, \frac{1}{3}, 1 \right) = \sqrt{3} E_{y,z} \left( 1, \frac{1}{3}, 1 \right) = -\frac{1}{2} \sqrt{3} E_{y,z} (T)$$

$$E_{x,xy} (1, \pm 1, 0) = \frac{1}{4} [\pm \sqrt{3} E_{x,x^2-y^2} (R) + E_{x,xy} (R) + 3 E_{y,x^2-y^2} (R) \pm \sqrt{3} E_{y,xy} (R)]$$

$$E_{x,xy} \left( 1, \frac{1}{3}, 1 \right) = \frac{1}{4} [E_{x,xy} (T) + 3 E_{y,x^2-y^2} (T)]$$

$$E_{x,xy} \left( 1, \frac{1}{3}, 1 \right) = \frac{1}{4} [E_{x,xz} (T) + 3 E_{y,yz} (T)]$$

$$E_{x,yz} \left( 1, \frac{1}{3}, 1 \right) = E_{y,xz} \left( 1, \frac{1}{3}, 1 \right) = \frac{1}{4} \sqrt{3} [-E_{x,xz} (T) + E_{y,yz} (T)]$$

$$E_{x,x^2-y^2} (1, \pm 1, 0) = \frac{1}{4} [-E_{x,x^2-y^2} (R) \pm \sqrt{3} E_{x,xy} (R) \pm \sqrt{3} E_{y,x^2-y^2} (R) + 3 E_{y,xy} (R)]$$

$$E_{x,x^2-y^2} \left( 1, \frac{1}{3}, 1 \right) = E_{y,xy} \left( 1, \frac{1}{3}, 1 \right) = \frac{1}{4} \sqrt{3} [-E_{x,xy} (T) + E_{y,x^2-y^2} (T)]$$

$$E_{x,3x^2-y^2} (1, \pm 1, 0) = \frac{1}{2} [E_{x,3x^2-y^2} (R) \pm \sqrt{3} E_{y,3x^2-y^2} (R)]$$

$$E_{x,3z^2-r^2} \left(1, \frac{1}{2}, 1\right) = \sqrt{3} E_{y,3z^2-r^2} \left(1, \frac{1}{3}, 1\right) = -\frac{1}{2} \sqrt{3} E_{y,3z^2-r^2} (T)$$

$$E_{y,xy} (1, \pm 1, 0) = \frac{1}{4} [3E_{x,x^2-y^2} (R) \pm \sqrt{3} E_{x,xy} (R) \mp \sqrt{3} E_{y,x^2-y^2} (R) - E_{y,xy} (R)]$$

$$E_{y,yz} \left(1, \frac{1}{3}, 1\right) = \frac{1}{4} [3 E_{x,xz} (T) + E_{y,yz} (T)]$$

$$E_{y,x^2-y^2} (1, \pm 1, 0) = \frac{1}{4} [\mp \sqrt{3} E_{x,x^2-y^2} (R) + 3 E_{x,xy} (R) + E_{y,x^2-y^2} (R) \mp \sqrt{3} E_{y,xy} (R)]$$

$$E_{y,x^2-y^2} \left(1, \frac{1}{3}, 1\right) = \frac{1}{4} [3 E_{x,xy} (T) + E_{y,x^2-y^2} (T)]$$

$$E_{y,3z^2-r^2} (1, \pm 1, 0) = \frac{1}{2} [\pm \sqrt{3} E_{x,3z^2-r^2} (R) - E_{y,3z^2-r^2} (R)]$$

$$E_{z,xy} \left(1, \frac{1}{3}, 1\right) = \sqrt{3} E_{z,x^2-y^2} \left(1, \frac{1}{3}, 1\right) = -\frac{1}{2} \sqrt{3} E_{z,x^2-y^2} (T)$$

$$E_{z,xz} (1, \pm 1, 0) = \frac{1}{2} [E_{z,xz} (R) \pm \sqrt{3} E_{z,yz} (R)]$$

$$E_{z,xz} \left(1, \frac{1}{3}, 1\right) = \sqrt{3} E_{z,yz} \left(1, \frac{1}{3}, 1\right) = -\frac{1}{2} \sqrt{3} E_{z,yz} (T)$$

$$E_{z,yz} (1, \pm 1, 0) = \frac{1}{2} [\pm \sqrt{3} E_{z,xz} (R) - E_{z,yz} (R)]$$

$$E_{xy,xy} (1, -1, 0) = \frac{1}{4} [E_{xy,xy} (R) + 3 E_{x^2-y^2,x^2-y^2} (R)]$$

$$E_{xy,xy} \left(1, \frac{1}{3}, 1\right) = \frac{1}{4} [E_{xy,xy} (T) + 3 E_{x^2-y^2,x^2-y^2} (T)]$$

$$E_{xz,xz} (1, -1, 0) = \frac{1}{4} [E_{xz,xz} (R) + 3 E_{yz,yz} (R)]$$

$$E_{xz,xz} \left(1, \frac{1}{3}, 1\right) = \frac{1}{4} [E_{xz,xz} (T) + 3 E_{yz,yz} (T)]$$

$$E_{yz,yz} (1, -1, 0) = \frac{1}{4} [E_{yz,yz} (R) + 3 E_{xz,xz} (R)]$$

$$E_{yz,yz} \left(1, \frac{1}{3}, 1\right) = \frac{1}{4} [E_{yz,yz} (T) + 3 E_{xz,xz} (T)]$$

$$E_{x^2-y^2, x^2-y^2} (1, -1, 0) = \frac{1}{4} [E_{x^2-y^2, x^2-y^2} (R) + 3E_{xy, xy} (R)]$$

$$E_{x^2-y^2, x^2-y^2} \left(1, \frac{1}{3}, 1\right) = \frac{1}{4} [E_{x^2-y^2, x^2-y^2} (T) + 3E_{xy, xy} (T)]$$

$$E_{xy, xz} \left(1, \frac{1}{3}, 1\right) = \frac{1}{4} [E_{xy, xz} (T) + 3E_{yz, x^2-y^2} (T)]$$

$$E_{xy, yz} \left(1, \frac{1}{3}, 1\right) = E_{xz, x^2-y^2} \left(1, \frac{1}{3}, 1\right) = \frac{1}{4} \sqrt{3} [E_{yz, x^2-y^2} (T) - E_{xy, xz} (T)]$$

$$E_{xy, x^2-y^2} (1, \pm 1, 0) = \mp \frac{1}{4} \sqrt{3} E_{x^2-y^2, x^2-y^2} (R) - E_{xy, x^2-y^2} (R) \pm \frac{1}{4} \sqrt{3} E_{xy, xy} (R)$$

$$E_{xy, x^2-y^2} \left(1, \frac{1}{3}, 1\right) = \frac{1}{4} \sqrt{3} [E_{x^2-y^2, x^2-y^2} (T) - E_{xy, xy} (T)]$$

$$E_{xy, 3z^2-r^2} (1, \pm 1, 0) = \frac{1}{2} [E_{xy, 3z^2-r^2} (R) \pm \sqrt{3} E_{x^2-y^2, 3z^2-r^2} (R)]$$

$$E_{xy, 3z^2-r^2} \left(1, \frac{1}{3}, 1\right) = \sqrt{3} E_{x^2-y^2, 3z^2-r^2} \left(1, \frac{1}{3}, 1\right) = -\frac{1}{2} \sqrt{3} E_{x^2-y^2, 3z^2-r^2} (T)$$

$$E_{yz, xz} (1, \pm 1, 0) = \pm \frac{1}{4} \sqrt{3} E_{xz, xz} (R) - E_{yz, xz} (R) \mp \frac{1}{4} \sqrt{3} E_{yz, yz} (R)$$

$$E_{yz, xz} \left(1, \frac{1}{3}, 1\right) = \frac{1}{4} \sqrt{3} [E_{yz, yz} (T) - E_{xz, xz} (T)]$$

$$E_{yz, x^2-y^2} \left(1, \frac{1}{3}, 1\right) = \frac{1}{4} [E_{yz, x^2-y^2} (T) + 3E_{xy, xz} (T)]$$

$$E_{xz, 3z^2-r^2} \left(1, \frac{1}{3}, 1\right) = \sqrt{3} E_{yz, 3z^2-r^2} \left(1, \frac{1}{3}, 1\right) = -\frac{1}{2} \sqrt{3} E_{yz, 3z^2-r^2} (T)$$

$$E_{x^2-y^2, 3z^2-r^2} (1, \pm 1, 0) = \frac{1}{2} [-E_{x^2-y^2, 3z^2-r^2} (R) \pm \sqrt{3} E_{xy, 3z^2-r^2} (R)]$$

We could use for  $R$  and  $T$  instead of  $(2, 0, 0)$  and  $(0, -2/3, 1)$  some other  $r_1$  and  $r_1 + t_2$  given above. We choose these particular  $R$  and  $T$  because the direction cosines  $(l, m, n)$  of these vectors are given by the most simple numbers possible. The matrix components expressed in terms of the three-center  $E$ -integrals in the nearest-neighbours approximation are summarized in Table III.



TABLE III

$(s/s)_{11}$	$E_{s,s}(0) + 2E_{s,s}(\mathbf{R}) (2 \cos \xi \cos \eta + \cos 2\xi)$
$(s/s)_{12}$	$2E_{s,s}(\mathbf{T}) \cos \zeta \left[ \left( 2 \cos \xi \cos \frac{1}{3} \eta + \cos \frac{2}{3} \eta \right) + i \left( 2 \cos \xi \sin \frac{1}{3} \eta - \sin \frac{2}{3} \eta \right) \right]$
$(s/x)_{11}$	$-2\sqrt{3} E_{s,y}(\mathbf{R}) \sin \xi \sin \eta + 2i E_{s,x}(\mathbf{R}) (\sin \xi \cos \eta + \sin 2\xi)$
$(s/x)_{12}$	$2\sqrt{3} E_{s,y}(\mathbf{T}) \sin \xi \cos \zeta \left( \sin \frac{1}{3} \eta - i \cos \frac{1}{3} \eta \right)$
$(s/y)_{11}$	$E_{s,y}(0) - 2E_{s,y}(\mathbf{R}) (\cos \xi \cos \eta - \cos 2\xi) + 2\sqrt{3} i E_{s,x}(\mathbf{R}) \cos \xi \sin \eta$
$(s/y)_{12}$	$-2E_{s,y}(\mathbf{T}) \cos \zeta \left[ \left( \cos \xi \cos \frac{1}{3} \eta - \cos \frac{2}{3} \eta \right) + i \left( \cos \xi \sin \frac{1}{3} \eta + \sin \frac{2}{3} \eta \right) \right]$
$(s/z)_{12}$	$-2E_{s,z}(\mathbf{T}) \sin \zeta \left[ \left( 2 \cos \xi \sin \frac{1}{3} \eta - \sin \frac{2}{3} \eta \right) - i \left( 2 \cos \xi \cos \frac{1}{3} \eta + \cos \frac{2}{3} \eta \right) \right]$
$(s/xy)_{11}$	$-2\sqrt{3} E_{s,x^2-y^2}(\mathbf{R}) \sin \xi \sin \eta + 2i E_{s,xy}(\mathbf{R}) (\sin \xi \cos \eta + \sin 2\xi)$
$(s/xy)_{12}$	$2\sqrt{3} E_{s,x^2-y^2}(\mathbf{T}) \sin \xi \cos \zeta \left( \sin \frac{1}{3} \eta - i \cos \frac{1}{3} \eta \right)$
$(s/yz)_{12}$	$2E_{s,yz}(\mathbf{T}) \sin \zeta \left[ \left( \cos \xi \sin \frac{1}{3} \eta + \sin \frac{2}{3} \eta \right) - i \left( \cos \xi \cos \frac{1}{3} \eta - \cos \frac{2}{3} \eta \right) \right]$
$(s/xz)_{12}$	$2\sqrt{3} E_{s,yz}(\mathbf{T}) \sin \xi \sin \zeta \left( \cos \frac{1}{3} \eta + i \sin \frac{1}{3} \eta \right)$
$(s/x^2 - y^2)_{11}$	$E_{s,x^2-y^2}(0) - 2E_{s,x^2-y^2}(\mathbf{R}) (\cos \xi \cos \eta - \cos 2\xi) + 2\sqrt{3} i E_{s,xy}(\mathbf{R}) \cos \xi \sin \eta$
$(s/x^2 - y^2)_{12}$	$-2E_{s,x^2-y^2}(\mathbf{T}) \cos \zeta \left[ \left( \cos \xi \cos \frac{1}{3} \eta - \cos \frac{2}{3} \eta \right) + i \left( \cos \xi \sin \frac{1}{3} \eta + \sin \frac{2}{3} \eta \right) \right]$
$(s/3z^2 - r^2)_{11}$	$E_{s,3z^2-r^2}(0) + 2E_{s,3z^2-r^2}(\mathbf{R}) (2 \cos \xi \cos \eta + \cos 2\xi)$
$(s/3z^2 - r^2)_{12}$	$2E_{s,3z^2-r^2}(\mathbf{T}) \cos \zeta \left[ \left( 2 \cos \xi \cos \frac{1}{3} \eta + \cos \frac{2}{3} \eta \right) + i \left( 2 \cos \xi \sin \frac{1}{3} \eta - \sin \frac{2}{3} \eta \right) \right]$
$(x/x)_{11}$	$E_{x,x}(0) + [E_{x,x}(\mathbf{R}) + 3E_{y,y}(\mathbf{R})] \cos \xi \cos \eta + 2E_{x,x}(\mathbf{R}) \cos 2\xi$
$(x/x)_{12}$	$\cos \zeta \left\{ [E_{x,x}(\mathbf{T}) + 3E_{y,y}(\mathbf{T})] \cos \xi \cos \frac{1}{2} \eta + 2E_{x,x}(\mathbf{T}) \cos \frac{2}{3} \eta \right\} + i \cos \xi \left\{ [E_{x,x}(\mathbf{T}) + 3E_{y,y}(\mathbf{T})] \cos \xi \sin \frac{1}{3} \eta - 2E_{x,x}(\mathbf{T}) \sin \frac{2}{3} \eta \right\}$

$$(x/y)_{11} \quad \sqrt{3} [E_{y,y}(\mathbf{R}) - E_{x,x}(\mathbf{R})] \sin \xi \sin \eta - 2i E_{x,y}(\mathbf{R}) (2 \sin \xi \cos \eta - \sin 2\xi)$$

$$(x/y)_{12} \quad \sqrt{3} [E_{x,x}(\mathbf{T}) - E_{y,y}(\mathbf{T})] \sin \xi \cos \zeta \left( \sin \frac{1}{3} \eta - i \cos \frac{1}{3} \eta \right)$$

$$(x/z)_{12} \quad 2\sqrt{3} E_{y,z}(\mathbf{T}) \sin \xi \sin \zeta \left( \cos \frac{1}{3} \eta + i \sin \frac{1}{3} \eta \right)$$

$$(x/xy)_{11} \quad E_{x,xy}(0) + [E_{x,xy}(\mathbf{R}) + 3 E_{y,x^2-y^2}(\mathbf{R})] \cos \xi \cos \eta + 2 E_{x,xy}(\mathbf{R}) \cos 2\xi + \\ \sqrt{3} i [E_{x,x^2-y^2}(\mathbf{R}) + E_{y,xy}(\mathbf{R})] \cos \xi \sin \eta$$

$$(x/xy)_{12} \quad \cos \zeta \left\{ [E_{x,xy}(\mathbf{T}) + 3 E_{y,x^2-y^2}(\mathbf{T})] \cos \xi \cos \frac{1}{3} \eta + 2 E_{x,xy}(\mathbf{T}) \cos \frac{2}{3} \eta \right\} + \\ + i \cos \zeta \left\{ [E_{x,xy}(\mathbf{T}) + 3 E_{y,x^2-y^2}(\mathbf{T})] \cos \xi \sin \frac{1}{3} \eta - 2 E_{x,xy}(\mathbf{T}) \sin \frac{2}{3} \eta \right\}$$

$$(x/yz)_{12} = (y/xz)_{12} \quad \sqrt{3} [E_{x,xz}(\mathbf{T}) - E_{y,yz}(\mathbf{T})] \sin \xi \sin \zeta \left( \cos \frac{1}{3} \eta + i \sin \frac{1}{3} \eta \right)$$

$$(x/xz)_{12} \quad \sin \zeta \left\{ - [E_{x,xz}(\mathbf{T}) + 3 E_{y,yz}(\mathbf{T})] \cos \xi \sin \frac{1}{3} \eta + 2 E_{x,xz}(\mathbf{T}) \sin \frac{2}{3} \eta \right\} \eta + \\ + i \sin \zeta \left\{ [E_{x,xz}(\mathbf{T}) + 3 E_{y,yz}(\mathbf{T})] \cos \xi \cos \frac{1}{3} \eta + 2 E_{x,xz}(\mathbf{T}) \cos \frac{2}{3} \eta \right\}$$

$$(x/x^2-y^2)_{11} \quad \sqrt{3} [E_{y,x^2-y^2}(\mathbf{R}) - E_{x,xy}(\mathbf{R})] \sin \xi \sin \eta - i \{ [E_{x,x^2-y^2}(\mathbf{R}) - \\ - 3 E_{y,xy}(\mathbf{R})] \sin \xi \cos \eta - 2 E_{x,x^2-y^2}(\mathbf{R}) \sin 2\xi \}$$

$$(x/x^2-y^2)_{12} = (y/xy)_{12} \quad \sqrt{3} [E_{x,xy}(\mathbf{T}) - E_{y,x^2}(\mathbf{T})] \sin \xi \cos \zeta \times \left( \sin \frac{1}{3} \eta - i \cos \frac{1}{3} \eta \right)$$

$$(x/3x^2-r^2)_{11} \quad -2\sqrt{3} E_{y,3x^2-r^2}(\mathbf{R}) \sin \xi \sin \eta + 2i E_{x,3x^2-r^2}(\mathbf{R}) (\sin \xi \cos \eta + \sin 2\xi)$$

$$(x/3x^2-r^2)_{12} \quad 2\sqrt{3} E_{y,3x^2-r^2}(\mathbf{T}) \sin \xi \cos \zeta \left( \sin \frac{1}{3} \eta - i \cos \frac{1}{3} \eta \right)$$

$$(y/y)_{11} \quad E_{y,y}(0) + [E_{y,y}(\mathbf{R}) + 3 E_{x,x}(\mathbf{R})] \cos \xi \cos \eta + 2 E_{y,y}(\mathbf{R}) \cos 2\xi$$

$$(y/y)_{12} \quad \cos \zeta \left\{ [E_{y,y}(\mathbf{T}) + 3 E_{x,x}(\mathbf{T})] \cos \xi \cos \frac{1}{3} \eta + 2 E_{y,y}(\mathbf{T}) \cos \frac{2}{3} \eta \right\} + \\ + i \cos \zeta \left\{ [E_{y,y}(\mathbf{T}) + 3 E_{x,x}(\mathbf{T})] \cos \xi \sin \frac{1}{3} \eta - 2 E_{y,y}(\mathbf{T}) \sin \frac{2}{3} \eta \right\}$$

$$(y/z)_{12} \quad 2 E_{y,z}(\mathbf{T}) \sin \zeta \left[ \left( \cos \xi \sin \frac{1}{3} \eta + \sin \frac{2}{3} \eta \right) - \right. \\ \left. - i \left( \cos \xi \cos \frac{1}{3} \eta - \cos \frac{2}{3} \eta \right) \right]$$

$$\begin{aligned}
(y/xy)_{11} & \quad \sqrt{3} [E_{y,x^2-y^2}(\mathbf{R}) - E_{x,xy}(\mathbf{R})] \sin \xi \sin \eta - \\
& \quad - i \{ [E_{y,xy}(\mathbf{R}) - 3 E_{x,x^2-y^2}(\mathbf{R})] \sin \xi \cos \eta - 2 E_{y,xy}(\mathbf{R}) \sin 2\xi \} \\
(y/yz)_{12} & \quad \sin \zeta \left\{ - [E_{y,yz}(\mathbf{T}) + 3 E_{x,xz}(\mathbf{T})] \cos \xi \sin \frac{1}{3} \eta + 2 E_{y,yz}(\mathbf{T}) \sin \frac{2}{3} \eta \right\} + \\
& \quad + i \sin \zeta \left\{ [E_{y,yz}(\mathbf{T}) + 3 E_{x,xz}(\mathbf{T})] \cos \xi \cos \frac{1}{3} \eta + 2 E_{y,yz}(\mathbf{T}) \cos \frac{2}{3} \eta \right\} \\
(y/x^2 - y^2)_{11} & \quad E_{y,x^2-y^2}(0) + [E_{y,x^2-y^2}(\mathbf{R}) + 3 E_{x,xy}(\mathbf{R})] \cos \xi \cos \eta + 2 E_{y,x^2-y^2}(\mathbf{R}) \cos 2\xi - \\
& \quad - \sqrt{3} i [E_{x,x^2-y^2}(\mathbf{R}) + E_{y,xy}(\mathbf{R})] \cos \xi \sin \eta \\
(y/x^2 - y^2)_{12} & \quad \cos \zeta \left\{ [E_{y,x^2-y^2}(\mathbf{T}) + 3 E_{x,xy}(\mathbf{T})] \cos \xi \cos \frac{1}{3} \eta + 2 E_{y,x^2-y^2}(\mathbf{T}) \cos \frac{2}{3} \eta \right\} + \\
& \quad + i \cos \zeta \left\{ [E_{y,x^2-y^2}(\mathbf{T}) + 3 E_{x,xy}(\mathbf{T})] \cos \xi \sin \frac{1}{3} \eta - 2 E_{y,x^2-y^2}(\mathbf{T}) \sin \frac{2}{3} \eta \right\} \\
(y/3z^2 - r^2)_{11} & \quad E_{y,3z^2-r^2}(0) - 2 E_{y,3z^2-r^2}(\mathbf{R}) (\cos \xi \cos \eta - \cos 2\xi) + 2\sqrt{3} i E_{x,3z^2-r^2}(\mathbf{R}) \cos \xi \sin \eta \\
(y/3z^2 - r^2)_{12} & \quad - 2 E_{y,3z^2-r^2}(\mathbf{T}) \cos \zeta \left[ \left( \cos \xi \cos \frac{1}{3} \eta - \cos \frac{2}{3} \eta \right) + i \left( \cos \xi \sin \frac{1}{3} \eta + \sin \frac{2}{3} \eta \right) \right] \\
(z/z)_{11} & \quad E_{z,z}(0) + 2 E_{z,z}(\mathbf{R}) (2 \cos \xi \cos \eta + \cos 2\xi) \\
(z/z)_{12} & \quad 2 E_{z,z}(\mathbf{T}) \cos \zeta \left[ \left( 2 \cos \xi \cos \frac{1}{3} \eta + \cos \frac{2}{3} \eta \right) + i \left( 2 \cos \xi \sin \frac{1}{3} \eta - \sin \frac{2}{3} \eta \right) \right] \\
(z/xy)_{12} & \quad 2\sqrt{3} E_{z,x^2-y^2}(\mathbf{T}) \sin \xi \sin \zeta \left( \cos \frac{1}{3} \eta + i \sin \frac{1}{3} \eta \right) \\
(z/yz)_{11} & \quad E_{z,yz}(0) - 2 E_{z,yz}(\mathbf{R}) (\cos \xi \cos \eta - \cos 2\xi) + 2\sqrt{3} i E_{x,xz}(\mathbf{R}) \cos \xi \sin \eta \\
(z/yz)_{12} & \quad - 2 E_{z,yz}(\mathbf{T}) \cos \zeta \left[ \left( \cos \xi \cos \frac{1}{3} \eta - \cos \frac{2}{3} \eta \right) + i \left( \cos \xi \sin \frac{1}{3} \eta + \sin \frac{2}{3} \eta \right) \right] \\
(z/xz)_{11} & \quad - 2\sqrt{3} E_{z,yz}(\mathbf{R}) \sin \xi \sin \eta + 2 i E_{z,xz}(\mathbf{R}) (\sin \xi \cos \eta + \sin 2\xi) \\
(z/xz)_{12} & \quad 2\sqrt{3} E_{z,yz}(\mathbf{T}) \sin \xi \cos \zeta \left( \sin \frac{1}{3} \eta - i \cos \frac{1}{3} \eta \right) \\
(z/x^2 - y^2)_{12} & \quad 2 E_{z,x^2-y^2}(\mathbf{T}) \sin \zeta \left[ \left( \cos \xi \sin \frac{1}{3} \eta + \sin \frac{2}{3} \eta \right) - i \left( \cos \xi \cos \frac{1}{3} \eta - \cos \frac{2}{3} \eta \right) \right] \\
(z/3z^2 - r^2)_{12} & \quad - 2 E_{z,3z^2-y^2}(\mathbf{T}) \sin \zeta \left[ \left( 2 \cos \xi \sin \frac{1}{3} \eta - \sin \frac{2}{3} \eta \right) - \right. \\
& \quad \left. - i \left( 2 \cos \xi \cos \frac{1}{3} \eta + \cos \frac{2}{3} \eta \right) \right]
\end{aligned}$$

$$\begin{aligned}
(xy/xy)_{11} & E_{xy,xy}(0) + [E_{xy,xy}(\mathbf{R}) + 3E_{x^2-y^2, x^2-y^2}(\mathbf{R})] \times \cos \xi \cos \eta + 2E_{xy,xy}(\mathbf{R}) \cos 2\xi \\
(xy/xy)_{12} & \cos \zeta \left\{ [E_{xy,xy}(\mathbf{T}) + 3E_{x^2-y^2, x^2-y^2}(\mathbf{T})] \cos \xi \cos \frac{1}{3} \eta + \right. \\
& + 2E_{xy,xy}(\mathbf{T}) \cos \frac{2}{3} \eta \left. \right\} + \\
& + i \cos \zeta \left\{ [E_{xy,xy}(\mathbf{T}) + 3E_{x^2-y^2, x^2-y^2}(\mathbf{T})] \cos \xi \sin \frac{1}{3} \eta - \right. \\
& - 2E_{xy,xy}(\mathbf{T}) \sin \frac{2}{3} \eta \left. \right\} \\
(xy/yz)_{12} & \sqrt{3} [E_{xy,xz}(\mathbf{T}) - E_{yz,x^2-y^2}(\mathbf{T})] \sin \xi \sin \zeta \left( \cos \frac{1}{3} \eta + i \sin \frac{1}{3} \eta \right) \\
= (xz/x^2 - y^2)_{12} & \\
(xy/xz)_{12} & \sin \zeta \left\{ - [E_{xy,xz}(\mathbf{T}) + 3E_{yz,x^2-y^2}(\mathbf{T})] \cos \xi \sin \frac{1}{3} \eta + \right. \\
& + 2E_{xy,xz}(\mathbf{T}) \sin \frac{2}{3} \eta \left. \right\} + \\
& + i \sin \zeta \left\{ [E_{xy,xz}(\mathbf{T}) + 3E_{yz,x^2-y^2}(\mathbf{T})] \cos \xi \cos \frac{1}{3} \eta + \right. \\
& + 2E_{xy,xz}(\mathbf{T}) \cos \frac{2}{3} \eta \left. \right\} \\
(xy/x^2 - y^2)_{11} & \sqrt{3} [E_{x^2-y^2, x^2-y^2}(\mathbf{R}) - E_{xy,xy}(\mathbf{R})] \sin \xi \sin \eta - \\
& - 2i E_{xy, x^2-y^2}(\mathbf{R}) (2 \sin \xi \cos \eta - \sin 2\xi) \\
(xy/x^2 - y^2)_{12} & \sqrt{3} [E_{xy,xy}(\mathbf{T}) - E_{x^2-y^2, x^2-y^2}(\mathbf{T})] \sin \xi \cos \zeta \times \\
& \times \left( \sin \frac{1}{3} \eta - i \cos \frac{1}{3} \eta \right) \\
(xy/3x^2 - r^2)_{11} & - 2\sqrt{3} E_{x^2-y^2, 3x^2-r^2}(\mathbf{R}) \sin \xi \sin \eta + 2i E_{xy, 3x^2-r^2}(\mathbf{R}) (\sin \xi \cos \eta + \sin 2\xi) \\
(xy/3x^2 - r^2)_{12} & 2\sqrt{3} E_{x^2-y^2, 3x^2-r^2}(\mathbf{T}) \sin \xi \cos \zeta \left( \sin \frac{1}{3} \eta - i \cos \frac{1}{3} \eta \right) \\
(yz/yz)_{11} & E_{yz,yz}(0) + [E_{yz,yz}(\mathbf{R}) + 3E_{xz,xz}(\mathbf{R})] \cos \xi \cos \eta + 2E_{yz,yz}(\mathbf{R}) \cos 2\xi \\
(yz/yz)_{12} & \cos \zeta \left\{ [E_{yz,yz}(\mathbf{T}) + 3E_{xz,xz}(\mathbf{T})] \cos \xi \cos \frac{1}{3} \eta + \right. \\
& + 2E_{yz,yz}(\mathbf{T}) \cos \frac{2}{3} \eta \left. \right\} +
\end{aligned}$$



$$\begin{aligned}
& + i \cos \zeta \left\{ [E_{yz,yz}(\mathbf{T}) + 3E_{xz,xz}(\mathbf{T})] \cos \xi \sin \frac{1}{3} \eta - \right. \\
& \quad \left. - 2E_{yz,yz}(\mathbf{T}) \sin \frac{2}{3} \eta \right\} \\
yz/xz)_{11} & \quad \sqrt{3} [E_{yz,yz}(\mathbf{R}) - E_{xz,xz}(\mathbf{R})] \sin \xi \sin \eta - \\
& \quad - 2i E_{yz,xz}(\mathbf{R}) (2 \sin \xi \cos \eta - \sin 2\xi) \\
(yz/xz)_{12} & \quad \sqrt{3} [E_{xz,xz}(\mathbf{T}) - E_{yz,yz}(\mathbf{T})] \sin \xi \cos \zeta \left( \sin \frac{1}{3} \eta - i \cos \frac{1}{3} \eta \right) \\
(yz/x^2 - y^2)_{12} & \quad \sin \zeta \left\{ - [E_{yz,x^2-y^2}(\mathbf{T}) + 3E_{xy,xz}(\mathbf{T})] \cos \xi \sin \frac{1}{3} \eta + \right. \\
& \quad \left. + 2E_{yz,x^2-y^2}(\mathbf{T}) \sin \frac{2}{3} \eta \right\} + \\
& \quad i \sin \zeta \left\{ [E_{yz,x^2-y^2}(\mathbf{T}) + 3E_{xy,xz}(\mathbf{T})] \cos \xi \cos \frac{1}{3} \eta + \right. \\
& \quad \left. + 2E_{yz,x^2-y^2}(\mathbf{T}) \cos \frac{2}{3} \eta \right\} \\
(yz/3z^2 - r^2)_{12} & \quad 2E_{yz,3z^2-r^2}(\mathbf{T}) \sin \zeta \left[ \left( \cos \xi \sin \frac{1}{3} \eta + \sin \frac{2}{3} \eta \right) - \right. \\
& \quad \left. - i \left( \cos \xi \cos \frac{1}{3} \eta - \cos \frac{2}{3} \eta \right) \right] \\
xz/xz)_{11} & \quad E_{xz,xz}(0) + [E_{xz,xz}(\mathbf{R}) + 3E_{yz,yz}(\mathbf{R})] \cos \xi \cos \eta + 2E_{xz,xz}(\mathbf{R}) \cos 2\xi \\
(xz/xz)_{12} & \quad \cos \zeta \left\{ [E_{xz,xz}(\mathbf{T}) + 3E_{yz,yz}(\mathbf{T})] \cos \xi \cos \frac{1}{3} \eta + \right. \\
& \quad \left. + 2E_{xz,xz}(\mathbf{T}) \cos \frac{2}{3} \eta \right\} + \\
& \quad + i \cos \zeta \left\{ [E_{xz,xz}(\mathbf{T}) + 3E_{yz,yz}(\mathbf{T})] \cos \xi \sin \frac{1}{3} \eta - \right. \\
& \quad \left. - 2E_{xz,xz}(\mathbf{T}) \sin \frac{2}{3} \eta \right\} \\
xz/3z^2 - r^2)_{12} & \quad 2\sqrt{3} E_{yz,3z^2-r^2}(\mathbf{T}) \sin \xi \sin \zeta \left( \cos \frac{1}{3} \eta + i \sin \frac{1}{3} \eta \right) \\
(x^2 - y^2/x^2 - y^2)_{11} & \quad E_{x^2-y^2,x^2-y^2}(0) + [E_{x^2-y^2,x^2-y^2}(\mathbf{R}) + 3E_{xy,xy}(\mathbf{R})] \times \\
& \quad \times \cos \xi \cos \eta + 2E_{x^2-y^2,x^2-y^2}(\mathbf{R}) \cos 2\xi
\end{aligned}$$

$$\begin{aligned}
& (x^2 - y^2/x^2 - y^2)_{12} \cos \zeta \left\{ [E_{x^2-y^2, x^2-y^2}(T) + 3 E_{xy, xy}(T)] \cos \xi \cos \frac{1}{3} \eta + \right. \\
& \quad \left. + 2 E_{x^2-y^2, x^2-y^2}(T) \cos \frac{2}{3} \eta \right\} + \\
& \quad + i \cos \zeta \left\{ [E_{x^2-y^2, x^2-y^2}(T) + 3 E_{xy, xy}(T)] \cos \xi \sin \frac{1}{3} \eta - \right. \\
& \quad \left. - 2 E_{x^2-y^2, x^2-y^2}(T) \sin \frac{2}{3} \eta \right\} \\
& (x^2 - y^2/3z^2 - r^2)_{11} E_{x^2-y^2, 3z^2-r^2}(0) - 2 E_{x^2-y^2, 3z^2-r^2}(R) (\cos \xi \cos \eta - \cos 2 \xi) + \\
& \quad + 2 \sqrt{3} i E_{xy, 3z^2-r^2}(R) \cos \xi \sin \eta \\
& (x^2 - y^2/3z^2 - r^2)_{12} - 2 E_{x^2-y^2, 3z^2-r^2}(T) \cos \zeta \left[ \left( \cos \xi \cos \frac{1}{3} \eta - \cos \frac{2}{3} \eta \right) + \right. \\
& \quad \left. + i \left( \cos \xi \sin \frac{1}{3} \eta + \sin \frac{2}{3} \eta \right) \right] \\
& (3z^2 - r^2/3z^2 - r^2)_{11} E_{3z^2-r^2, 3z^2-r^2}(0) + 2 E_{3z^2-r^2, 3z^2-r^2}(R) (2 \cos \xi \cos \eta + \cos 3 \xi) \\
& (3z^2 - r^2/3z^2 - r^2)_{12} 2 E_{3z^2-r^2, 3z^2-r^2}(T) \cos \zeta \left[ \left( 2 \cos \xi \cos \frac{1}{3} \eta + \cos \frac{2}{3} \eta \right) + \right. \\
& \quad \left. + i \left( 2 \cos \xi \sin \frac{1}{3} \eta - \sin \frac{2}{3} \eta \right) \right]
\end{aligned}$$

The  $E$ -integrals for  $r_l \neq 0$  can be written in the following form:

$$\begin{aligned}
E_{m,n}(r_l) &= \int \varphi_m^*(r) H \varphi_n(r - r_l) dr \\
&= \int \varphi_m^*(r) [-\Delta + U(r) + U(r - r_l)] \varphi_n(r - r_l) dr + \\
& \quad + \sum_{i \neq l, 0} \int \varphi_m^*(r) U(r - r_j) \varphi_n(r - r_l) dr + \\
& \quad + \sum_i \int \varphi_m^*(r) U(r - r_j - t_2) \varphi_n(r - r_l) dr,
\end{aligned}$$

in which the second and third term contain only three-center integrals. We now make the approximation of neglecting all three-center integrals. The  $E$ -integrals for  $r = 0$  in the two-center approximation can be written

$$E_{m,n}(0) = \int \varphi_m^*(r) [-\Delta + U(r) + \sum_j U(r - r_j) + \sum_j U(r - r_j - t_2)] \varphi_n(r) dr,$$

where  $r_j$  and  $r_j + t_2$  are here the position vectors of the 12 nearest neighbours.

Slater and Koster have given a table for the reduction of  $E$ -integrals to two-center integrals calculated for functions with  $\sigma$ -,  $\pi$ -,  $\delta$ -symmetry. In the two-center

approximation only 16 independent integrals remain:  $s_0, p_0, d_0, d_1, d_2, (pd)_0, (ss\sigma)_1, (sp\sigma)_1, (sd\sigma)_1, (pp\sigma)_1, (pd\sigma)_1, (pd\pi)_1, (dd\sigma)_1, (dd\pi)_1, (dd\delta)_1$ . Using Table I of Slater and Koster we must know only the directions cosines of the vectors  $\mathbf{R}$  and  $\mathbf{T}$ .

We have for  $\mathbf{R}$ :  $l = 1, m = 0, n = 0$  and for  $\mathbf{T}$ :  $l = 0, m = -\sqrt{3}/3, n = \sqrt{2}/3$

The  $E$ -integrals in terms of the two-center integrals are given in Table IV.

TABLE IV

$$E_{s,y}(O) = E_{s,x^2-y^2}(O) = E_{s,3z^2-r^2}(O) = E_{x,yz}(O) = E_{y,3z^2-r^2}(O) = E_{x^2-y^2,3z^2-r^2}(O) = 0$$

$$E_{s,y}(\mathbf{R}) = E_{s,xy}(\mathbf{R}) = E_{x,y}(\mathbf{R}) = E_{x,xy}(\mathbf{R}) = E_{y,x^2-y^2}(\mathbf{R}) = E_{y,3z^2-r^2}(\mathbf{R}) = E_{z,yz}(\mathbf{R}) \\ = E_{xy,x^2-y^2}(\mathbf{R}) = E_{xy,3z^2-r^2}(\mathbf{R}) = E_{yz,xz}(\mathbf{R}) = 0$$

$$E_{s,s}(\mathbf{R}) = s_0$$

$$E_{x,x}(O) = E_{y,y}(O) = E_{z,z}(O) = p_0$$

$$E_{xy,xy}(O) = E_{x^2-y^2,x^2-y^2}(O) = d_0$$

$$E_{xz,xz}(O) = E_{yz,yz}(O) = d_1$$

$$E_{3x^2-r^2,3z^2-r^2}(O) = d_2$$

$$E_{x,xy}(O) = E_{y,x^2-y^2}(O) = (pd)_0$$

$$E_{s,s}(\mathbf{R}) = E_{s,s}(\mathbf{T}) = (ss\sigma)_1$$

$$E_{s,x}(\mathbf{R}) = -\sqrt{3} E_{s,y}(\mathbf{T}) = \sqrt{\frac{3}{2}} E_{s,z}(\mathbf{T}) = (sp\sigma)_1$$

$$E_{s,3z^2-r^2}(\mathbf{T}) = -E_{s,3z^2-r^2}(\mathbf{R}) = -\sqrt{3} E_{s,x^2-y^2}(\mathbf{T}) = \frac{1}{3} \sqrt{3} E_{s,x^2-y^2}(\mathbf{R}) = \\ = -\frac{1}{2} \sqrt{\frac{3}{2}} E_{s,yz}(\mathbf{T}) = \frac{1}{2} (sd\sigma)_1$$

$$E_{x,x}(\mathbf{R}) = (pp\sigma)_1$$

$$E_{x,x}(\mathbf{T}) = E_{y,y}(\mathbf{R}) = E_{z,z}(\mathbf{R}) = (pp\pi)_1$$

$$E_{y,y}(\mathbf{T}) = \frac{1}{3} (pp\sigma)_1 + \frac{2}{3} (pp\pi)_1$$

$$E_{z,z}(\mathbf{T}) = \frac{2}{3} (pp\sigma)_1 + \frac{1}{3} (pp\pi)_1$$

$$E_{y,z}(\mathbf{T}) = -\frac{1}{3} \sqrt{2} (pp\sigma)_1 + \frac{1}{3} \sqrt{2} (pp\pi)_1$$

$$E_{z,xz}(\mathbf{R}) = -\sqrt{3} E_{x,xy}(\mathbf{T}) = \sqrt{\frac{3}{2}} E_{x,xz}(\mathbf{T}) = E_{y,xy}(\mathbf{R}) = (pd\pi)_1$$

$$E_{x,3z^2-r^2}(R) = -\frac{1}{3}\sqrt{3}E_{x,x^2-y^2}(R) = -\frac{1}{2}(pd\sigma)_1$$

$$E_{y,yz}(T) = \frac{1}{3}\sqrt{2}(pd\sigma)_1 + \frac{1}{3}\sqrt{\frac{2}{3}}(pd\pi)_1$$

$$E_{y,x^2-y^2}(T) = \frac{1}{6}(pd\sigma)_1 + \frac{2}{9}\sqrt{3}(pd\pi)_1$$

$$E_{y,3z^2-r^2}(T) = -\frac{1}{6}\sqrt{3}(pd\sigma)_1 + \frac{2}{3}(pd\pi)_1$$

$$E_{z,yz}(T) = -\frac{2}{3}(pd\sigma)_1 + \frac{1}{9}\sqrt{3}(pd\pi)_1$$

$$E_{z,x^2-y^2}(T) = -\frac{1}{6}\sqrt{2}(pd\sigma)_1 + \frac{1}{3}\sqrt{\frac{2}{3}}(pd\pi)_1$$

$$E_{z,3z^2-r^2}(T) = \frac{1}{2}\sqrt{\frac{2}{3}}(pd\sigma)_1 + \frac{1}{3}\sqrt{2}(pd\pi)_1$$

$$E_{xy,xy}(R) = E_{xz,xz}(R) = (dd\pi)_1$$

$$E_{yz,yz}(R) = (dd\delta)_1$$

$$E_{xy,xy}(T) = \frac{1}{3}(dd\pi)_1 + \frac{2}{3}(dd\delta)_1$$

$$E_{xz,xz}(T) = \frac{2}{3}(dd\pi)_1 + \frac{1}{3}(dd\delta)_1$$

$$E_{yz,yz}(T) = \frac{2}{3}(dd\sigma)_1 + \frac{1}{9}(dd\pi)_1 + \frac{2}{9}(dd\delta)_1$$

$$E_{x^2-y^2,x^2-y^2}(R) = \frac{3}{4}(dd\sigma)_1 + \frac{1}{4}(dd\delta)_1$$

$$E_{x^2-y^2,x^2-y^2}(T) = \frac{1}{12}(dd\sigma)_1 + \frac{2}{9}(dd\pi)_1 + \frac{25}{36}(dd\delta)_1$$

$$E_{3x^2-r^2,3z^2-r^2}(R) = \frac{1}{4}(dd\sigma)_1 + \frac{3}{4}(dd\delta)_1$$

$$E_{3x^2-r^2,3z^2-r^2}(T) = \frac{1}{4}(dd\sigma)_1 + \frac{2}{3}(dd\pi)_1 + \frac{1}{12}(dd\delta)_1$$

$$E_{xy,xz}(T) = -\frac{1}{3}\sqrt{2}(dd\pi)_1 + \frac{1}{3}\sqrt{2}(dd\delta)_1$$

$$E_{yz,x^2-y^2}(T) = \frac{1}{6}\sqrt{2}(dd\sigma)_1 + \frac{1}{9}\sqrt{2}(dd\pi)_1 - \frac{5}{18}\sqrt{2}(dd\delta)_1$$



$$E_{yz,3z^2-r^2}(T) = -\frac{1}{2} \sqrt{\frac{2}{3}} (dd\sigma)_1 + \frac{1}{3} \sqrt{\frac{2}{3}} (dd\pi)_1 + \frac{1}{6} \sqrt{\frac{2}{3}} (dd\delta)_1$$

$$E_{x^2-y^2,3z^2-r^2}(R) = -\frac{1}{4} \sqrt{3} (dd\sigma)_1 = \frac{1}{4} \sqrt{3} (dd\delta)_1$$

$$E_{x^2-y^2,3z^2-r^2}(T) = -\frac{1}{12} \sqrt{3} (dd\sigma)_1 + \frac{2}{9} \sqrt{3} (dd\pi)_1 - \frac{5}{56} \sqrt{3} (dd\delta)_1$$

The table given by Slater and Koster simplifies also considerably the calculations of the overlap integrals:

$$\int \varphi_m^*(\mathbf{r}-\mathbf{r}_i) \varphi_n(\mathbf{r}-\mathbf{r}_j) d\mathbf{r}.$$

We summarize finally in Table V the matrix components of energy in the two-center approximation.

TABLE V

$(s/s)_{11}$	$s_0 + 2(ss\sigma)_1 (2 \cos \xi \cos \eta + \cos 2 \xi)$
$(s/s)_{12}$	$2(ss\sigma)_1 \cos \zeta \left[ \left( 2 \cos \xi \cos \frac{1}{3} \eta + \cos \frac{2}{3} \eta \right) + \right. \\ \left. + i \left( 2 \cos \xi \sin \frac{1}{3} \eta - \sin \frac{2}{3} \eta \right) \right]$
$(s/x)_{11}$	$2i(sp\sigma)_1 (\sin \xi \cos \eta + \sin 2 \xi)$
$(s/x)_{12}$	$-2(sp\sigma)_1 \sin \xi \cos \zeta \left( \sin \frac{1}{3} \eta - i \cos \frac{1}{3} \eta \right)$
$(s/y)_{11}$	$2\sqrt{3} i(sp\sigma)_1 \cos \xi \sin \eta$
$(s/y)_{12}$	$\frac{2}{3} \sqrt{3} (sp\sigma)_1 \cos \zeta \left[ \left( \cos \xi \cos \frac{1}{3} \eta - \cos \frac{2}{3} \eta \right) + \right. \\ \left. + i \left( \cos \xi \sin \frac{1}{3} \eta + \sin \frac{2}{3} \eta \right) \right]$
$(s/z)_{12}$	$-2 \sqrt{\frac{2}{3}} (sp\sigma)_1 \sin \zeta \left[ \left( 2 \cos \xi \sin \frac{1}{3} \eta - \sin \frac{2}{3} \eta \right) - \right. \\ \left. - i \left( 2 \cos \xi \cos \frac{1}{3} \eta + \cos \frac{2}{3} \eta \right) \right]$
$(s/xy)_{11}$	$-3(sd\sigma)_1 \sin \xi \sin \eta$
$(s/xy)_{12}$	$-(sd\sigma)_1 \sin \xi \cos \zeta \left( \sin \frac{1}{3} \eta - i \cos \frac{1}{3} \eta \right)$

$$\begin{aligned}
(s/yx)_{12} & -2 \sqrt{\frac{2}{3}} (sd\sigma)_1 \sin \zeta \left[ \left( \cos \xi \sin \frac{1}{3} \eta + \sin \frac{2}{3} \eta \right) - \right. \\
& \quad \left. - i \left( \cos \xi \cos \frac{1}{3} \eta - \cos \frac{2}{3} \eta \right) \right] \\
(s/xz)_{12} & -2 \sqrt{2} (sd\sigma)_1 \sin \xi \sin \zeta \left( \cos \frac{1}{3} \eta + i \sin \frac{1}{3} \eta \right) \\
(s/x^2 - y^2)_{11} & -\sqrt{3} (sd\sigma)_2 (\cos \xi \cos \eta - \cos 2\xi) \\
(s/x^2 - y^2)_{12} & \frac{1}{3} \sqrt{3} (sd\sigma)_1 \cos \zeta \left[ \left( \cos \xi \cos \frac{1}{3} \eta - \cos \frac{2}{3} \eta \right) + \right. \\
& \quad \left. + i \left( \cos \xi \sin \frac{1}{3} \eta + \sin \frac{2}{3} \eta \right) \right] \\
(s/3z^2 - r^2)_{11} & - (sd\sigma)_1 (2 \cos \xi \cos \eta + \cos 2\xi) \\
(s/3z^2 - r^2)_{12} & (sd\sigma)_1 \cos \zeta \left[ \left( 2 \cos \xi \cos \frac{1}{3} \eta + \cos \frac{2}{3} \eta \right) + \right. \\
& \quad \left. + i \left( 2 \cos \xi \sin \frac{1}{3} \eta - \sin \frac{2}{3} \eta \right) \right] \\
(x/x)_{11} & p_0 + [(pp\sigma)_1 + 3 (pp\pi)_1] \cos \xi \cos \eta + 2 (pp\sigma)_1 \cos 2\xi \\
(x/x)_{12} & \cos \zeta \left\{ [(pp\sigma)_1 + 3 (pp\pi)_1] \cos \xi \cos \frac{1}{3} \eta + 2 (pp\pi)_1 \cos \frac{2}{3} \eta \right\} + \\
& \quad + i \cos \zeta \left\{ [(pp\sigma)_1 + 3 (pp\pi)_1] \cos \xi \sin \frac{1}{3} \eta - 2 (pp\pi)_1 \sin \frac{2}{3} \eta \right\} \\
(x/y)_{11} & -\sqrt{3} [(pp\sigma)_1 - (pp\pi)_1] \sin \xi \sin \eta \\
(x/y)_{12} & -\frac{1}{3} \sqrt{3} [(pp\sigma)_1 - (pp\pi)_1] \sin \xi \cos \zeta \left( \sin \frac{1}{3} \eta - i \cos \frac{1}{3} \eta \right) \\
(x/z)_{12} & -2 \sqrt{\frac{2}{3}} [(pp\sigma)_1 - (pp\pi)_1] \sin \xi \sin \zeta \left( \cos \frac{1}{3} \eta + i \sin \frac{1}{3} \eta \right) \\
(x/xy)_{11} & (pd)_0 + i \left[ \frac{2}{3} (pd\sigma)_1 + \sqrt{3} (pd\pi)_1 \right] \cos \xi \sin \eta \\
(x/xy)_{12} & \cos \zeta \left\{ \left[ \frac{1}{2} (pd\sigma)_1 + \frac{1}{3} \sqrt{3} (pd\pi)_1 \right] \cos \xi \cos \frac{1}{3} \eta - \right. \\
& \quad \left. - \frac{2}{3} \sqrt{3} (pd\pi)_1 \cos \frac{2}{3} \eta \right\} + \\
& \quad + i \cos \zeta \left\{ \left[ \frac{1}{2} (pd\sigma)_1 + \frac{1}{3} \sqrt{3} (pd\pi)_1 \right] \cos \xi \sin \frac{1}{3} \eta + \right. \\
& \quad \left. + \frac{2}{3} \sqrt{3} (pd\pi)_1 \sin \frac{2}{3} \eta \right\}
\end{aligned}$$

$$\begin{aligned} (x/yz)_{12} &= (y/xz)_{12} \\ &= (z/xy)_{12} \end{aligned} \quad - \left[ \sqrt{\frac{2}{3}} (pd\sigma)_1 - \frac{2}{3} \sqrt{2} (pd\pi)_1 \right] \sin \xi \sin \zeta \left( \cos \frac{1}{3} \eta + i \sin \frac{1}{3} \eta \right)$$

$$\begin{aligned} (x/xz)_{12} \quad & \sin \zeta \left\{ - \left[ \sqrt{2} (pd\sigma)_1 + 2 \sqrt{\frac{2}{3}} (pd\pi)_1 \right] \cos \xi \sin \frac{1}{3} \eta + \right. \\ & + 2 \sqrt{\frac{2}{3}} (pd\pi)_1 \sin \frac{2}{3} \eta \left. \right\} + \\ & + i \sin \zeta \left\{ \left[ \sqrt{2} (pd\sigma)_1 + 2 \sqrt{\frac{2}{3}} (pd\pi)_1 \right] \cos \xi \cos \frac{1}{3} \eta + \right. \\ & + 2 \sqrt{\frac{2}{3}} (pd\pi)_1 \cos \frac{2}{3} \eta \left. \right\} \end{aligned}$$

$$(x/x^2 - y^2)_{11} \quad i \left\{ - \left[ \frac{1}{2} \sqrt{3} (pd\sigma)_1 - 3 (pd\pi)_1 \right] \sin \xi \cos \eta + \sqrt{3} (pd\sigma)_1 \sin 2 \xi \right\}$$

$$\begin{aligned} (x/x^2 - y^2)_{12} \\ = (y/xy)_{12} \end{aligned} \quad - \frac{1}{3} \left[ \frac{1}{2} \sqrt{3} (pd\sigma)_1 + 5 (pd\pi)_1 \right] \sin \xi \cos \zeta \left( \sin \frac{1}{3} \eta - i \cos \frac{1}{3} \eta \right)$$

$$(x/3z^2 - r^2)_{11} \quad - i (pd\sigma)_1 (\sin \xi \cos \eta + \sin 2 \xi)$$

$$(x/3z^2 - r^2)_{12} \quad - \left[ (pd\sigma)_1 - \frac{4}{3} \sqrt{3} (pd\pi)_1 \right] \sin \xi \cos \zeta \left( \sin \frac{1}{3} \eta - i \cos \frac{1}{3} \eta \right)$$

$$(y/y)_{11} \quad P_0 + [3 (pp\sigma)_1 + (pp\pi)_1] \cos \xi \cos \eta + 2 (pp\pi)_1 \cos 2 \xi$$

$$\begin{aligned} (y/y)_{12} \quad & \frac{1}{3} \cos \zeta \left\{ [(pp\sigma)_1 + 11 (pp\pi)_1] \cos \xi \cos \frac{1}{3} \eta + \right. \\ & + 2 [(pp\sigma)_1 + 2 (pp\pi)_1] \cos \frac{2}{3} \eta \left. \right\} + \\ & + \frac{1}{3} i \cos \zeta \left\{ [(pp\sigma)_1 + 11 (pp\pi)_1] \cos \xi \sin \frac{1}{3} \eta - \right. \\ & - 2 [(pp\sigma)_1 + 2 (pp\pi)_1] \sin \frac{2}{3} \eta \left. \right\} \end{aligned}$$

$$\begin{aligned} (y/z)_{12} \quad & - \frac{2}{3} \sqrt{2} [(pp\sigma)_1 - (pp\pi)_1] \sin \zeta \left[ \left( \cos \xi \sin \frac{1}{3} \eta + \sin \frac{2}{3} \eta \right) - \right. \\ & - i \left( \cos \xi \cos \frac{1}{3} \eta - \cos \frac{1}{3} \eta \right) \left. \right] \end{aligned}$$

$$(y/xy)_{11} \quad i \left\{ \left[ \frac{3}{2} \sqrt{3} (pd\sigma)_1 - (pd\pi)_1 \right] \sin \xi \cos \eta + 2 (pd\pi)_1 \sin 2 \xi \right\}$$

$$(y/yz)_{12} \quad \frac{1}{3} \sin \zeta \left\{ - \left[ \sqrt{2} (pd\sigma)_1 + 10 \sqrt{\frac{2}{3}} (pd\pi)_1 \right] \cos \xi \sin \frac{1}{3} \eta + \right.$$

$$\begin{aligned}
& + 2 \left[ \sqrt{2} (pd\sigma)_1 + \sqrt{\frac{2}{3}} (pd\pi)_1 \right] \sin \frac{2}{3} \eta \Big\} + \\
& + \frac{1}{3} i \sin \zeta \left\{ \left[ \sqrt{2} (pd\sigma)_1 + 10 \sqrt{\frac{2}{3}} (pd\pi)_1 \right] \cos \xi \cos \frac{1}{3} \eta + \right. \\
& \left. + 2 \left[ \sqrt{2} (pd\sigma)_1 + \frac{2}{3} (pd\pi)_1 \right] \cos \frac{2}{3} \eta \right\} \\
(y/x^2 - y^2)_{11} & (pd)_0 - i \left[ \frac{3}{2} (pd\sigma)_1 + \sqrt{3} (pd\pi)_1 \right] \cos \xi \sin \eta \\
(y/x^2 - y^2)_{12} & \frac{1}{3} \cos \zeta \left\{ \left[ \frac{1}{2} (pd\sigma)_1 - \frac{7}{3} \sqrt{3} (pd\pi)_1 \right] \cos \xi \cos \frac{1}{3} \eta + \right. \\
& + 2 \left[ \frac{1}{2} (pd\sigma)_1 + \frac{2}{3} \sqrt{3} (pd\pi)_1 \right] \cos \frac{2}{3} \eta \Big\} + \\
& + \frac{1}{3} i \cos \zeta \left\{ \left[ \frac{1}{2} (pd\sigma)_1 - \frac{7}{3} \sqrt{3} (pd\pi)_1 \right] \cos \xi \sin \frac{1}{3} \eta - \right. \\
& \left. - 2 \left[ \frac{1}{2} (pd\sigma)_1 + \frac{2}{3} \sqrt{3} (pd\pi)_1 \right] \sin \frac{2}{3} \eta \right\} \\
(y/3x^2 - r^2)_{11} & - \sqrt{3} i (pd\sigma)_2 \cos \xi \sin \eta \\
(y/3x^2 - r^2)_{12} & \frac{1}{3} \left[ \sqrt{3} (pd\sigma)_1 - 4 (pd\pi)_1 \right] \cos \zeta \left[ \left( \cos \xi \cos \frac{1}{3} \eta - \cos \frac{2}{3} \eta \right) + \right. \\
& \left. + i \left( \cos \xi \sin \frac{1}{3} \eta + \sin \frac{2}{3} \eta \right) \right] \\
(z/x)_{11} & p_0 + 2 (pp\pi)_1 (2 \cos \xi \cos \eta + \cos 2\xi) \\
(z/x)_{12} & \frac{2}{3} \left[ 2 (pp\sigma)_2 + (pp\pi)_1 \right] \cos \zeta \left[ \left( 2 \cos \xi \cos \frac{1}{3} \eta + \cos \frac{2}{3} \eta \right) + \right. \\
& \left. + i \left( 2 \cos \xi \sin \frac{1}{3} \eta - \sin \frac{2}{3} \eta \right) \right] \\
(z/yx)_{11} & 2\sqrt{3} i (pd\pi)_1 \cos \xi \sin \eta \\
(z/yx)_{12} & \frac{2}{3} \left[ 2 (pd\sigma)_1 - \frac{1}{3} \sqrt{3} (pd\pi)_1 \right] \cos \zeta \left[ \left( \cos \xi \cos \frac{1}{3} \eta - \cos \frac{2}{3} \eta \right) + \right. \\
& \left. + i \left( \cos \xi \sin \frac{1}{3} \eta + \sin \frac{2}{3} \eta \right) \right] \\
(z/xx)_{11} & 2 i (pd\pi)_1 (\sin \xi \cos \eta + \sin 2\xi) \\
(z/xx)_{12} & - \frac{2}{3} [2\sqrt{3} (pd\sigma)_1 - (pd\pi)_1] \sin \xi \cos \zeta \left( \sin \frac{1}{3} \eta - i \cos \frac{1}{3} \eta \right)
\end{aligned}$$



$$\begin{aligned}
(z/x^2 - y^2)_{12} &= -\frac{1}{3} \left[ \sqrt{2} (pd\sigma)_1 - 2 \sqrt{\frac{2}{3}} (pd\pi)_1 \right] \sin \zeta \left[ \left( \cos \xi \sin \frac{1}{3} \eta + \sin \frac{2}{3} \eta \right) - \right. \\
&\quad \left. - i \left( \cos \xi \cos \frac{1}{3} \eta - \cos \frac{2}{3} \eta \right) \right] \\
(z/3z^2 - r^2)_{12} &= - \left[ \sqrt{\frac{2}{3}} (pd\sigma)_1 + \frac{2}{3} \sqrt{2} (pd\pi)_1 \right] \sin \zeta \left[ \left( 2 \cos \xi \sin \frac{1}{3} \eta + \sin \frac{2}{3} \eta \right) - \right. \\
&\quad \left. - i \left( 2 \cos \xi \cos \frac{1}{3} \eta + \cos \frac{2}{3} \eta \right) \right] \\
(xy/xy)_{11} &= d_0 + \left[ \frac{9}{4} (dd\sigma)_1 + (dd\pi)_1 + \frac{3}{4} (dd\delta)_1 \right] \cos \xi \cos \eta + 2 (dd\pi)_1 \cos 2\xi \\
(xy/xy)_{12} &= \cos \zeta \left\{ \frac{1}{4} [(dd\sigma)_1 + 4 (dd\pi)_1 + 11 (dd\delta)_1] \cos \xi \cos \frac{1}{3} \eta + \right. \\
&\quad \left. + \frac{2}{3} [(dd\pi)_1 + 2 (dd\delta)_1] \cos \frac{2}{3} \eta \right\} + \\
&\quad + i \cos \zeta \left\{ \frac{1}{4} [(dd\sigma)_1 + 4 (dd\pi)_1 + 11 (dd\delta)_1] \cos \xi \sin \frac{1}{3} \eta - \right. \\
&\quad \left. - \frac{2}{3} [(dd\pi)_1 + 2 (dd\delta)_1] \sin \frac{2}{3} \eta \right\} \\
(xy/yz)_{12} &= (xz/x^2 - y^2)_{12} = - \sqrt{\frac{2}{3}} \left[ \frac{1}{2} (dd\sigma)_1 + \frac{4}{3} (dd\pi)_1 - \frac{11}{6} (dd\delta)_1 \right] \sin \xi \sin \zeta \times \\
&\quad \times \left( \cos \frac{1}{3} \eta + i \sin \frac{1}{3} \eta \right) \\
(xy/xz)_{12} &= - \sqrt{2} \sin \zeta \left\{ \frac{1}{2} [(dd\sigma)_1 - (dd\delta)_1] \cos \xi \sin \frac{1}{3} \eta + \right. \\
&\quad \left. + \frac{2}{3} [(dd\pi)_1 - (dd\delta)_1] \sin \frac{2}{3} \eta \right\} + \\
&\quad + \sqrt{2} i \sin \zeta \left\{ \frac{1}{2} [(dd\sigma)_1 - (dd\delta)_1] \cos \xi \cos \frac{1}{3} \eta - \right. \\
&\quad \left. - \frac{2}{3} [(dd\pi)_1 - (dd\delta)_1] \cos \frac{2}{3} \eta \right\} \\
(xy/x^2 - y^2)_{11} &= \frac{1}{4} \sqrt{3} [3 (dd\sigma)_1 - 4 (dd\pi)_1 + (dd\delta)_1] \sin \xi \sin \eta \\
(xy/x^2 - y^2)_{12} &= -\frac{1}{3} \sqrt{3} \left[ \frac{1}{4} (dd\sigma)_1 - \frac{1}{3} (dd\pi)_1 + \frac{1}{12} (dd\delta)_1 \right] \sin \xi \cos \zeta \times \\
&\quad \times \left( \sin \frac{1}{3} \eta - i \cos \frac{1}{3} \eta \right)
\end{aligned}$$

$$\begin{aligned}
(xy/3z^2 - r^2)_{11} & \quad \frac{3}{2} [(dd\sigma)_1 - (dd\delta)_1] \sin \xi \sin \eta \\
(xy/3z^2 - r^2)_{12} & \quad - \left[ \frac{1}{2} (dd\sigma)_1 - \frac{4}{3} (dd\pi)_1 + \frac{5}{6} (dd\delta)_1 \right] \sin \xi \cos \xi \times \\
& \quad \times \left( \sin \frac{1}{3} \eta - i \cos \frac{1}{3} \eta \right) \\
(yz/yz)_{11} & \quad d_1 + [3 (dd\pi)_1 + (dd\delta)_1] \cos \xi \cos \eta + 2 (dd\delta)_1 \cos 2 \xi \\
(yz/yz)_{12} & \quad \frac{1}{3} \cos \xi \left\{ \left[ 2 (dd\sigma)_1 + \frac{19}{3} (dd\pi)_1 + \frac{11}{3} (dd\delta)_1 \right] \cos \xi \cos \frac{1}{3} \eta + \right. \\
& \quad + 2 \left[ 2 (dd\sigma)_1 + \frac{1}{3} (dd\pi)_1 + \frac{2}{3} (dd\delta)_1 \right] \cos \frac{2}{3} \eta \left. \right\} + \\
& \quad + \frac{1}{3} i \cos \xi \left\{ \left[ 2 (dd\sigma)_1 + \frac{19}{3} (dd\pi)_1 + \frac{11}{3} (dd\delta)_1 \right] \times \cos \xi \sin \frac{1}{3} \eta - \right. \\
& \quad - 2 \left[ 2 (dd\sigma)_1 + \frac{1}{3} (dd\pi)_1 + \frac{2}{3} (dd\delta)_1 \right] \sin \frac{2}{3} \eta \left. \right\} \\
(yz/xz)_{11} & \quad - \sqrt{3} [(dd\pi)_1 - (dd\delta)_1] \sin \xi \sin \eta \\
(yz/xz)_{12} & \quad - \frac{1}{3} \sqrt{3} \left[ 2 (dd\sigma)_1 - \frac{5}{3} (dd\pi)_1 - \frac{1}{3} (dd\delta)_1 \right] \sin \xi \cos \xi \times \\
& \quad \times \left( \sin \frac{1}{3} \eta - i \cos \frac{1}{3} \eta \right) \\
(yz/x^2 - y^2)_{12} & \quad - \frac{1}{3} \sqrt{2} \sin \xi \left\{ \left[ \frac{1}{2} (dd\sigma)_1 - \frac{8}{3} (dd\pi)_1 + \frac{13}{6} (dd\delta)_1 \right] \cos \xi \sin \frac{1}{3} \eta - \right. \\
& \quad - \left[ (dd\sigma)_1 + \frac{2}{3} (dd\pi)_1 - \frac{5}{3} (dd\delta)_1 \right] \sin \frac{2}{3} \eta \left. \right\} + \\
& \quad + \frac{1}{3} \sqrt{2} i \sin \xi \left\{ \left[ \frac{1}{2} (dd\sigma)_1 - \frac{8}{3} (dd\pi)_1 + \frac{13}{6} (dd\delta)_1 \right] \cos \xi \cos \frac{1}{3} \eta + \right. \\
& \quad + \left[ (dd\sigma)_1 + \frac{2}{3} (dd\pi)_1 - \frac{5}{3} (dd\delta)_1 \right] \cos \frac{2}{3} \eta \left. \right\} \\
(yz/3z - r^2)_{12} & \quad - 2 \sqrt{\frac{2}{3}} \left[ \frac{1}{2} (dd\sigma)_1 - \frac{1}{3} (dd\pi)_1 - \frac{1}{6} (dd\delta)_1 \right] \sin \xi \times \\
& \quad \times \left[ \left( \cos \xi \sin \frac{1}{3} \eta + \sin \frac{2}{3} \eta \right) + i \left( \cos \xi \cos \frac{1}{3} \eta - \cos \frac{2}{3} \eta \right) \right] \\
(xz/xz)_{11} & \quad d_1 + [(dd\pi)_1 + 3 (dd\delta)_1] \cos \xi \cos \eta + 2 (dd\pi)_1 \cos 2 \xi
\end{aligned}$$

$$\begin{aligned}
(xz/xz)_{12} & \cos \zeta \left\{ [2 (dd\sigma)_1 + (dd\pi)_1 + (dd\delta)_1] \cos \xi \cos \frac{1}{3} \eta + \right. \\
& \quad \left. + \frac{2}{3} [2 (dd\pi)_1 + (dd\delta)_1] \cos \frac{2}{3} \eta \right\} + \\
& \quad + i \cos \zeta \left\{ [2 (dd\sigma)_1 + (dd\pi)_1 + (dd\delta)_1] \cos \xi \sin \frac{1}{3} \eta - \right. \\
& \quad \left. - \frac{2}{3} [2 (dd\pi)_1 + (dd\delta)_1] \sin \frac{2}{3} \eta \right\} \\
(xz/3z^2 - r^2)_{12} & - 2 \sqrt{2} \left[ \frac{1}{2} (dd\sigma)_1 - \frac{1}{3} (dd\pi)_1 - \frac{1}{6} (dd\delta)_1 \right] \sin \xi \sin \zeta \times \\
& \quad \times \left( \cos \frac{1}{3} \eta + i \sin \frac{1}{3} \eta \right) \\
(x^2 - y^2/x^2 - y^2)_{11} & d_0 + \left[ \frac{3}{4} (dd\sigma)_1 + 3 (dd\pi)_1 + \frac{1}{4} (dd\delta)_1 \right] \cos \xi \cos \eta + \\
& \quad + \frac{1}{2} [3 (dd\sigma)_1 + (dd\delta)_1] \cos 2 \xi \\
(x^2 - y^2/x^2 - y^2)_{12} & \frac{1}{3} \cos \zeta \left\{ \left[ \frac{1}{4} (dd\sigma)_1 + \frac{11}{3} (dd\pi)_1 + \frac{97}{12} (dd\delta)_1 \right] \cos \xi \cos \frac{1}{3} \eta + \right. \\
& \quad + 2 \left[ \frac{1}{4} (dd\sigma)_1 + \frac{2}{3} (dd\pi)_1 + \frac{25}{12} (dd\delta)_1 \right] \cos \frac{2}{3} \eta \Big\} + \\
& \quad + \frac{1}{3} i \cos \zeta \left\{ \left[ \frac{1}{4} (dd\sigma)_1 + \frac{11}{13} (dd\pi)_1 + \frac{97}{12} (dd\delta)_1 \right] \times \cos \xi \sin \frac{1}{3} \eta - \right. \\
& \quad \left. - 2 \left[ \frac{1}{4} (dd\sigma)_1 + \frac{2}{3} (dd\pi)_1 + \frac{25}{12} (dd\delta)_1 \right] \sin \frac{2}{3} \eta \right\} \\
(x^2 - y^2/3z^2 - r^2)_{11} & \frac{1}{2} \sqrt{3} [(dd\sigma)_1 - (dd\delta)_1] (\cos \xi \cos \eta - \cos 2 \xi) \\
(x^2 - y^2/3z^2 - r^2)_{12} & \frac{2}{3} \sqrt{3} \left[ \frac{1}{4} (dd\sigma)_1 - \frac{2}{3} (dd\pi)_1 + \frac{5}{12} (dd\delta)_1 \right] \cos \zeta \times \\
& \quad \times \left[ \left( \cos \xi \cos \frac{1}{3} \eta - \cos \frac{2}{3} \eta \right) + i \left( \cos \xi \sin \frac{1}{3} \eta + \sin \frac{2}{3} \eta \right) \right] \\
(3z^2 - r^2/3z^2 - r^2)_{11} & d_2 + \frac{1}{2} [(dd\sigma)_1 + 3 (dd\delta)_1] (2 \cos \xi \cos \eta + \cos 2 \xi) \\
(3z^2 - r^2/3z^2 - r^2)_{12} & \left[ \frac{1}{2} (dd\sigma)_1 + \frac{4}{3} (dd\pi)_1 + \frac{1}{6} (dd\delta)_1 \right] \cos \zeta \times \\
& \quad \times \left[ \left( 2 \cos \xi \cos \frac{1}{3} \eta + \cos \frac{2}{3} \eta \right) + i \left( 2 \cos \xi \sin \frac{1}{3} \eta - \sin \frac{2}{3} \eta \right) \right]
\end{aligned}$$

It should hardly be emphasized that all the above tables can be also used for the reduction of general overlap integrals of Bloch sums.

The author wish to thank Dr. M. Suffczyński for suggesting the theme of the present work and for valuable discussions.

#### КРАТКОЕ СОДЕРЖАНИЕ

М. Мьонсек, *Применение метода тесной связи для исследования свойств симметрии энергетических полос в компактной гексагональной структуре.*

В работе высчитано элементы матриц энергии сперва при применении интегралов трицентровых а после при приближении двуцентровом. В расчетах было принято во внимание только первых соседей сетки.

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# PI-SIGMA INTERACTION IN THE FREE-ELECTRON MODEL. I. THEORY.

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The method of antisymmetrized molecular orbitals for the three-dimensional free-electron model was developed here for the case of linear conjugated molecules. In this model the  $\pi$  and  $\sigma$  electrons are assumed to form a gas in one cylindrical box extending along the molecular core, and both groups of electrons are characterized according to the classification given originally by Nikitine and Komoss. Then the whole  $\pi - \sigma$  interaction can be treated directly, contrary to the treatment of this problem in the Goeppert-Mayer-Sklar scheme.

The values of the electronic repulsion integrals presented by the author in an earlier work for the case of the so called "one-dimensional" free-electron model, were verified as corresponding to the integrals of the present scheme when the radius of the box tends to zero.

## 1. Introduction

As a further step in the development of the theory of the free-electron model, we may consider two problems which are quite important, if we want to undertake more advanced investigations of absorption spectra by means of this model. The problems are:

- a) what is the influence of the interaction between the more stable (steady)  $\sigma$ -electrons and the  $\pi$ -electrons on the spectrum of the molecule;
- b) how do the transversal box dimensions affect the resulting location of energy states.

Before giving the mathematical scheme of our treatment of the above problems, let us recollect briefly the basic ideas of the  $\pi - \sigma$  interaction calculations in the LCAO MO theory. These ideas were recently discussed very keenly by Stewart (1956) and the present report on them is based mainly on the results of his work.

The characteristic feature of the AS LCAO MO method is, that although the  $\pi$  electron states are described in this method exclusively by means of the molecular orbitals constructed from  $2p$  atomic orbitals, the other wave functions of the  $L$ -shell are also taken into account in computing the energies corresponding to those molecular orbitals.

In view of this fact it is not permissible to consider the results of the LCAO method as related to  $\pi$  electrons only, for we have here an irresolvable "intermixing" of  $\pi$  and  $\sigma$  electron energies caused by the existence of interaction integrals between the  $\pi$  electrons and the core. Therefore in the Goeppert-Mayer-Sklar theory we cannot speak about the energy of a  $\pi$  electron system in an exact sense. It is also not possible in this scheme to obtain correct values for the differences of the total electronic energy of the molecule, owing to the inadequate determination of the core potential.

Thus, in order to obtain a correct description of molecular electronic states the entire  $\pi$  and  $\sigma$  electron system should be examined. The point nuclear charges with  $1s$  electrons might then be taken as the core. The inclusion of  $\sigma$  orbitals into the AS LCAO MO scheme in order to perform  $\pi - \sigma$  interaction calculations is of no avail, in such a meaning that the  $\sigma$  electrons just play an important role in determining the electronic energies and eigenfunctions (through the choice of  $Z$ ) of the  $\pi$  electrons themselves.

Hence, the conclusion of Ross (1952) and Moser (1953) that the  $\pi - \sigma$  interaction, in the meaning discussed there, is small enough to be neglected is not sufficiently established. We know only that the  $\pi - \sigma$  interaction energy is to a great extent automatically included in the standard ASMO calculations of the electron states. In this scheme, we know, for instance (Stewart), that the share of the  $\pi - \sigma$  Coulomb energy in the whole interaction energy in ethylene states amounts to about ten times that of the  $\pi - \pi$  Coulomb and exchange interaction energies.

So, we see that the Goeppert-Mayer-Sklar scheme — as developed by Ross and Moser — cannot be used at all to investigate the  $\pi - \sigma$  interaction effects. Thus, an attempt should be made to build up a theory, in which the interaction between  $\sigma$  and  $\pi$  electrons can be directly and fully (i. e. all the  $\pi - \pi$ ,  $\pi - \sigma$  and  $\sigma - \sigma$  interactions) taken into account. This corresponds to a computational scheme in which  $\pi$  and  $\sigma$  eigenenergies and eigenfunctions are separated and completely independent from each other, in the sense that in the  $\pi$  eigenfunctions and energies there is no reference to  $\sigma$ , and vice versa.

It may be noted that each of the three types of interactions mentioned above can then be treated separately.

## 2. Treatment of the Problem

Nikitine and Komoss have given, in the author's opinion, a reasonable method of describing  $\pi$  and  $\sigma$  electrons in molecules with a conjugated double-bond system based on the theory of the free-electron model. They have assumed, similarly to treatment of  $\pi$  electrons thus far in the free-electron model scheme, that the  $\sigma$  electrons belonging to the single and double C—C bonds of the chain form a gas. Nevertheless, the both gases are characterized differently in view of their geometrical distribution and energetical relations.

Let us consider, following Nikitine and Komoss, the solution of the Schroedinger

equation for free electrons in a cylindrical box of the length  $L$  with a straightened chain of carbon atoms as the axis; we assume, in addition, that the potential inside the box is equal to zero. The solution has then the general form: (for a non-branched box; the conditions that the wave functions vanish at the ends of the free-electron path being satisfied):

$$\varphi_{n,l,q}(\vec{r}) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} z N_{l,q} J_l(u_{l,q}r) \cos l\vartheta \quad (1)$$

The energy eigenvalues are:

$$E_{n,l} = \frac{\hbar^2}{8m} \left( \frac{u_{l,q}^2}{\pi^2} + \frac{n^2}{L^2} \right) \quad (2)$$

( $N_{l,q}$  — normalization factor in  $r, \vartheta$  variables).

Next it was assumed that solutions of the  $J_0$ -type correspond to  $\sigma$  electrons and solutions of the  $J_1$ -type to  $\pi$  electrons. Such a treatment is not only in agreement with the energetical classification of both electron groups, i. e. for a given  $n, q$  state a higher energy corresponds to the  $\pi$  than to the  $\sigma$  electrons but, it has also two additional features:

1) — for both electron groups it is not necessary to assume a priori any spatial restrictions in the  $r$  direction, since these restrictions are already contained in solutions (1): the constants  $u_{0,q}$  and  $u_{1,q}$  can be chosen in such a way that  $J_0$  and  $J_1$  vanish simultaneously on the cylinder's edge, and the first zero points were taken as those beyond which both functions vanish. (Henceforth we shall omit the index  $q$  in the wave functions as equal everywhere to 1).

2) — when  $u_0$  and  $u_1$  are chosen in the above manner, the eigenfunction of  $\sigma$  electrons, at the point where the radial function of the  $\pi$  electrons ( $J_1$ ) attains a maximum, assumes approximately the same value. The radial function of  $\sigma$  electrons has its maximum on the cylinder axis. Both functions, as already mentioned, vanish simultaneously for  $r = R$ . ( $R$  denotes the radius of the tube).

Thus, the above solution to our problem has the following simple physical interpretation: the  $\pi$  electrons are "solved" in the  $\sigma$  electron "sea", and the  $\sigma$  cloud is most dense on the axis of C—C bonds; the  $\pi$  electron cloud has its density maximum approximately at half the distance between the axis and the side-wall of the box. At the place where the maximum of the  $\pi$  electron density occurs, the  $\sigma$  density is, although only roughly, as large as that of  $\pi$  electrons.

The picture described above is qualitatively in very good agreement with the analysis of the mutual relation between  $\sigma$  and  $\pi$  densities made by Coulson et al. (1951). In the essential points both descriptions are, in fact, identical; hence the application of the Nikitine-Komoss model to  $\pi - \sigma$  investigations seemed to be especially convenient.

Most important is the fact that now we may perform the calculations for the many-electron problem where the  $\pi$  and  $\sigma$  states are characterized independently

and the total mutual interaction between the electrons is directly treated. In this way we avoid the internal contradictions discussed in the introduction which arise in the calculation of  $\pi$  and  $\sigma$  states when we start from assumptions involved in the methods based on computations with LCAO orbitals.

We have the Hamiltonian in the form:

$$H = - \sum_{\mu} \frac{\hbar^2}{2m} \nabla_{\mu}^2 + \sum_{\mu < \nu} \frac{e^2}{r_{\mu\nu}} \quad (3)$$

where  $\nabla^2$  should be taken in cylindrical coordinates. The eigenfunctions in the zero-order approximation for  $\sigma$  and  $\pi$  electrons are those of formula (1), with indices  $n, 0$  and  $n, 1$ , respectively. We construct the antisymmetrized wave function for the whole system of both electron groups by assuming that the  $\pi$  and  $\sigma$  pairs occupy, successively, the energy states beginning with the lowest. In the case of e. g. polyenes with  $N$  carbon atoms in the chain, we have  $2(N-1)$  electrons in the  $\sigma$ -group (on  $N-1$  levels) and  $N$   $\pi$  electrons (on  $N/2$  levels). The electrons from the C—H bonds are strongly localized and are mostly outside the  $\pi$  electron "sea" — hence we do not include them into the  $\pi$ — $\sigma$  gas of our problem. We also assume, similarly to Ross and Moser, that the interaction of these electrons with the electron pairs of the C—C bonds is not essentially significant. Thus, the wave function of our  $s$ -electron problem ( $s = 3N-2$  for polyenes) will be composed of antisymmetrized products of the type ( $\alpha, \beta$  — spin eigenfunctions):

$$(s!)^{-\frac{1}{2}} \left| \begin{array}{ll} (\varphi_{1,0} \alpha)_{\sigma}^1 (\varphi_{1,0} \beta)_{\sigma}^1 (\varphi_{2,0} \alpha)_{\sigma}^1 \dots & (\varphi_{1,1} \alpha)_{\sigma}^1 (\varphi_{1,1} \beta)_{\sigma}^1 (\varphi_{2,1} \alpha)_{\sigma}^1 \dots \\ (\varphi_{1,0} \alpha)_{\sigma}^2 (\varphi_{1,0} \beta)_{\sigma}^2 (\varphi_{2,0} \alpha)_{\sigma}^2 \dots & (\varphi_{1,1} \alpha)_{\sigma}^2 (\varphi_{1,1} \beta)_{\sigma}^2 (\varphi_{2,1} \alpha)_{\sigma}^2 \dots \\ \dots & \dots \\ \dots & \dots \\ (\varphi_{1,0} \alpha)_{\pi}^1 (\varphi_{1,0} \beta)_{\pi}^1 (\varphi_{2,0} \alpha)_{\pi}^1 \dots & (\varphi_{1,1} \alpha)_{\pi}^1 (\varphi_{1,1} \beta)_{\pi}^1 (\varphi_{2,1} \alpha)_{\pi}^1 \dots \\ (\varphi_{1,0} \alpha)_{\pi}^2 (\varphi_{1,0} \beta)_{\pi}^2 (\varphi_{2,0} \alpha)_{\pi}^2 \dots & (\varphi_{1,1} \alpha)_{\pi}^2 (\varphi_{1,1} \beta)_{\pi}^2 (\varphi_{2,1} \alpha)_{\pi}^2 \dots \\ \dots & \dots \\ \dots & \dots \end{array} \right| \quad (4)$$

The energies of the states and the excitation energies can now be computed according to the generally known scheme; in addition, let us remember, that now only the  $\pi$ — $\pi$  and  $\sigma$ — $\sigma$  transitions are permissible.  $\pi$ — $\sigma$  transitions, as Nikitine and Komoss have shown, are forbidden.

Now in the scheme developed above it remains only to give the formulas for the electronic interaction integrals. We shall have three types of these integrals. In the Coulomb integrals case; for instance, they are:

$$J_{n,m} = \iint \varphi_{n,i}^*(\mathbf{r}) \varphi_{m,i'}^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \varphi_{n,i}(\mathbf{r}) \varphi_{m,i'}(\mathbf{r}') d\tau d\tau' \quad (5)$$



and correspond for  $l = l' = 0$  to  $\sigma - \sigma$  interaction,

for  $l = 0, l' = 1$  or vice versa — to  $\pi - \sigma$  interaction,

and for  $l = l' = 1$  — to  $\pi - \pi$  interaction.

We obtain three types of exchange integrals in a similar way.

It is also possible, in our treatment, to take the configurational interaction into account. Then the index system of  $\varphi$  in the electronic repulsion integrals becomes, in general, completely irregular. This, however, as we shall see, does not lead to any additional complications in the calculations.

### 3. Calculation of Interaction Integrals

Each of the Coulomb or exchange integrals may be very easily reduced — as it was been done previously (Olszewski 1955 — henceforth referred to as I) — to the calculation of integrals of the type

$$C = \frac{e^2}{L^2} N_l^2 N_{l'}^2 \int_0^L \int_0^L \cos a z \cos c z' dz dz' \int_0^R \int_0^R J_l(u_l r) \left\{ \begin{array}{c} J_{l'}(u_{l'} r') J_l(u_l r) \\ \text{or} \\ J_l(u_l r') J_{l'}(u_{l'} r) \end{array} \right\} \times$$

$$\times J_{l'}(u_{l'} r') r r' dr dr' \int_0^{2\pi} \int_0^{2\pi} \cos l \vartheta \left[ \begin{array}{c} \cos l' \vartheta' \cos l \vartheta \\ \text{or} \\ \cos l \vartheta' \cos l' \vartheta \end{array} \right] \cos l' \vartheta' d\vartheta d\vartheta' \frac{e^2}{r_{12}} \quad (6)$$

where  $r_{12} = |r - r'|$ , and  $l, l'$  are independently 0 or 1.

Now let us make use of the fundamental relation (Ivanenko and Sokolov 1951):

$$C = \int \varrho(\mathbf{r}) \Phi(\mathbf{r}) d\mathbf{r} = \int \int \varrho(\mathbf{r}) \cdot 4\pi G(\mathbf{r}, \mathbf{r}') \varrho'(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (7)$$

where  $\Phi$  is the electric potential of  $\varrho'(\mathbf{r}')$ , and  $G$  is the Green function of a three-dimensional Laplace-Poisson equation, i. e. satisfying the equation

$$\nabla^2 G = -\delta(\mathbf{r} - \mathbf{r}') \quad (8)$$

In eq. (7)  $\varrho$  and  $\varrho'$  are the products of the functions appearing in the  $C$  integral, in (6) and are dependent on  $r, \vartheta, z$  and  $r', \vartheta', z'$  respectively.

Next, we rewrite  $\delta(\mathbf{r} - \mathbf{r}')$  in cylindrical coordinates

$$\delta(\mathbf{r} - \mathbf{r}') = \delta(z - z') \cdot \frac{\delta(r - r')}{r'} \cdot \delta(\vartheta - \vartheta') \quad (9)$$

and, further, we represent  $\delta(z - z')$  and  $\delta(r - r')$  in the form of the expansions:



$$\delta(z - z') = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\kappa|z-z'|} d\kappa \quad (10)$$

$$\frac{\delta(r - r')}{r'} = \int_0^{\infty} k \cdot J_0(kr) J_0(kr') dk \quad (11)$$

(Let us remember, that the relation  $\delta(r - r') = \sqrt{\frac{r'}{r}} \delta(r - r')$  holds).

Dividing (8) by the  $\nabla^2$  operator, we obtain finally<sup>1,2</sup>:

$$G = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \frac{e^{i\kappa|z-z'|}}{k^2 + \kappa^2} d\kappa \int_0^{\infty} k J_0(kr) J_0(kr') dk \cdot \delta(\vartheta - \vartheta') \quad (12)$$

Now we may introduce the expression for  $G$  into (6) and perform the integration. Unfortunately, it is not possible to complete the integration of  $C$ . Nevertheless we obtain a result which can be relatively easily treated numerically.

We have<sup>3</sup> (for  $c \neq a$ ):

$$\begin{aligned} \frac{C}{e^2} = N_l^2 N_{l'}^2 \int_0^{\pi} \int_0^R \int_0^R & \left[ \frac{\pi}{2} \cdot \frac{\cos^2(c+a) \frac{L}{2}}{c+a} \{I_0(\tilde{\omega}c) - L_0(\tilde{\omega}c) + I_0(\tilde{\omega}a) - \right. \\ & \left. - L_0(\tilde{\omega}a)\} + \frac{\pi}{2} \cdot \frac{\cos^2(c-a) \frac{L}{2}}{c-a} \{I_0(\tilde{\omega}c) - L_0(\tilde{\omega}c) - I_0(\tilde{\omega}a) + L_0(\tilde{\omega}a)\} + \right. \end{aligned}$$

<sup>1</sup> The absolute value  $|z - z'|$  in the Fourier expansion of  $\delta(z - z')$  ensures that the sign of the exponential coefficient does not change and thus makes possible the integration.

<sup>2</sup> It is a fact of essential importance that when the full  $\delta(r - r')$  expansion is used we may interchange the order of integration over  $z, z'$  with the integration over  $k$  (and over  $\kappa$ ) as a result of the presence of the product  $J_0(kr) J_0(kr')$ ; then the double integral over  $\kappa, k$  in  $G$  is uniformly convergent in the whole  $z, z'$  region. However in the AS FEMO method, previously developed in I, we have also made calculations with the three-dimensional wave functions of the FE model, and of course, with the corresponding Green function for the interaction potential, but it was assumed next, that the potential acts in one direction; i. e. along the free-electron path. Then the Green function takes the form:

$$G' = \frac{1}{4\pi|z - z'|} = \frac{1}{8\pi^3} \int_{-\infty}^{+\infty} \frac{e^{i\kappa|z-z'|}}{\kappa^2 + k^2} d\kappa \int_0^{\infty} k dk \int_0^{2\pi} d\theta \quad (13)$$

Here, however,  $G'$ , is divergent for  $z = z'$  and the interchange of the order of integration over  $k, \kappa$  with that over  $z, z'$  is not permissible. However, see further the next section.

<sup>3</sup> The sign of  $C$  corresponds to the absolute values taken for the interaction integrals.

$$\begin{aligned}
& + [\cos cL + \cos aL] \cdot \left\{ \frac{c^2}{c^2 - a^2} \left( \frac{1}{c} \cos cL \left[ Si(cL) - \frac{\pi}{2} \right] I_0(\tilde{\omega}c) - M(\tilde{\omega}c) \right) + \right. \\
& \quad \left. - \frac{a^2}{c^2 - a^2} \left( \frac{1}{a} \cos aL \left[ Si(aL) - \frac{\pi}{2} \right] I_0(\tilde{\omega}a) - M(\tilde{\omega}a) \right) \right\} \times \\
& \quad \times \frac{1}{L^2} \cdot \frac{2D}{\pi} J_0(u_l r) \left\{ \begin{array}{c} J_{l'}(u_{l'} r) \quad J_l(u_l r) \\ \text{or} \\ J_l(u_l r) \quad J_{l'}(u_{l'} r) \end{array} \right\} J_{l'}(u_{l'} r') r r' dr dr' d\chi; \quad (14)
\end{aligned}$$

for  $c = a$

$$\begin{aligned}
\frac{C}{e^2} &= N_l^2 N_{l'}^2 \int_0^\pi \int_0^R \int_0^R \left[ \frac{\pi}{2} \cdot \frac{1}{a} \{ I_0(\tilde{\omega}a) - L_0(\tilde{\omega}a) \} \cos^2 aL + \right. \\
& \quad + \frac{\pi}{2} \cdot \frac{1}{a} \left\{ \tilde{\omega}a I_1(\tilde{\omega}a) - \tilde{\omega}a \left[ L_1(\tilde{\omega}a) + \frac{1}{\Gamma\left(\frac{3}{2}\right)\Gamma\left(\frac{1}{2}\right)} \right] \right\} + \\
& \quad + 2 \cos aL \left\{ \cos aL \left[ Si(aL) - \frac{\pi}{2} \right] [I_0(\tilde{\omega}a) + \tilde{\omega}a I_1(\tilde{\omega}a)] \cdot \frac{1}{2a} - \right. \\
& \quad \left. \left. - M(\tilde{\omega}a) - \frac{a}{2} \frac{dM(\tilde{\omega}a)}{da} \right] \right\} \times \\
& \quad \times \frac{1}{L^2} \cdot \frac{2D}{\pi} \cdot J_l(u_l r) \{ \quad \} J_{l'}(u_{l'} r') r r' dr dr' d\chi; \quad (15)
\end{aligned}$$

for  $c = a = 0$ :

$$\begin{aligned}
\frac{C}{e^2} &= N_l^2 N_{l'}^2 \int_0^\pi \int_0^R \int_0^R \left[ \pi L - \frac{\pi \tilde{\omega}}{\Gamma\left(\frac{3}{2}\right)\Gamma\left(\frac{1}{2}\right)} - M(0) \right] \times \\
& \quad \times \frac{1}{L^2} \frac{2D}{\pi} J_l(u_l r) \cdot \{ \quad \} J_{l'}(u_{l'} r') r r' dr dr' d\chi \quad (16)
\end{aligned}$$

where we have introduced the following notation<sup>4,5</sup>:

$$\tilde{\omega} = (r^2 + r'^2 - 2rr' \cos \chi)^{1/2}$$

$$I_\nu(\tilde{\omega}a) = \sum_{m=0}^{\infty} \frac{\left(\frac{1}{2} \tilde{\omega}a\right)^{\nu+2m}}{m! \Gamma(\nu+m+1)} \quad \text{--- Bessel function of the second kind}$$

$$L_r(\tilde{\omega} a) = \sum_{m=0}^{\infty} \frac{\left(\frac{1}{2} \tilde{\omega} a\right)^{r+2m+1}}{\Gamma(m+\frac{3}{2})\Gamma(r+m+\frac{3}{2})} - \text{Struve function of the second kind}$$

$$M(\tilde{\omega} a) = \frac{1}{a} \sum_1^{\infty} m \sum_m^{\infty} n (-1)^m \frac{[2(m-1)]!}{(aL)^{2m-1}} (\tilde{\omega} a)^{2n} \frac{1}{(n!)^2}$$

$$\left( \text{for large } a, M(\tilde{\omega} a) \text{ tends rapidly to } -\frac{1}{a^2 L} [I_0(\tilde{\omega} a) - 1] \right).$$

For the Bessel function product in { }, (and for the cosine product in [ ] in Eq. (6)), we take upper or lower row for Coulomb or exchange integrals respectively.

$D$  is a constant equal to

$$2\pi \text{ when } l = l' = 0 \quad (\sigma - \sigma \text{ interaction}) \quad (18a)$$

$$\pi \text{ when } l = 0, l' = 1 \text{ or } l = 1, l' = 0 \quad (\pi - \sigma \text{ interaction}) \quad (18b)$$

$$\frac{3}{4}\pi \text{ when } l = l' = 1 \quad (\pi - \pi \text{ interaction}) \quad (18c)$$

In the computation of the above integrals the vanishing of the wave functions at the ends of the free-electron path was taken into account. In addition, we note that when the configurational interaction is included in our scheme, there may appear in the matrix elements integrals of a type different from those calculated above. They have, under the integral sign, the form of the following expression corresponding to the product of "transversal" factors of the wave functions of our problem:

$$J_l(u_r) J_{l'}(u_r r') J_{l'}(u_r r') J_{l'}(u_r r') \cos l\vartheta \cos l'\vartheta' \cos l'\vartheta \cos l'\vartheta' \quad (19)$$

where  $l, l'$  can be 0 or 1 independently one of another. Such integrals, as may readily be seen, vanish for  $l \neq l'$  as a result of the integration over  $\vartheta, \vartheta'$ . Thus only integrals of the  $C$  type will appear in calculations for which the configurational interaction is included.

It is characteristic that the numerical values of the interaction integrals depend exclusively on two quantities taken from beyond the theoretical scheme, the length  $L$  and the radius  $R$  of the box. The first is defined usually by the chemical formula of

<sup>4</sup>  $N_l, N_{l'}$  are the normalization factors of the  $r, \vartheta$  functions in the above scheme (Nikitine and Komoss), and have values:

$$N_0 = \frac{1}{\sqrt{2\pi}} \frac{2.724}{R}; \quad N_1 = \frac{1}{\sqrt{\pi}} \frac{3.514}{R}$$

<sup>5</sup> Employing Sonine's formula

$$\int_0^{\pi} I_0(\tilde{\omega} a) d\chi = \pi I_0(ar) J_0(ar')$$

where  $r > r'$ , we may at once integrate over  $\chi$  in the  $C$  term with  $I_0(\tilde{\omega} a)$  or  $I_0(\tilde{\omega} c)$  in the integrand. However, this does not seem to facilitate the numerical calculations.

the molecule and then the experimental values on the C—C distances are taken into account, the second one can be estimated either on the basis of the considerations of Nikitine and Komoss, or from formulae given by Kuhn and Huber (1953). In the latter case  $R$  is connected with the effective nuclear charge of the carbon atoms, being ( $R$ ) inversely proportional to  $Z$ . However, for larger molecules, the criteria of Nikitine and Komoss lead to contradictions. Besides, in their method the values confining  $R$  change considerably with a change in the chain length; this is especially so in the case of polyenes.

In our treatment of the problem it seems most reasonable to take  $Z$  equal to four. For such value of  $Z$  the radius of the box would be confined, according to Kuhn and Huber, to lie between 1.15 Å and 1.35 Å, assuming that the side-wall is placed on the boundary of  $\pi$  electron cloud. This value of  $R$  is in very good agreement with that obtained by Nikitine and Komoss for the first homologues of symmetrical cyanines.

#### 4. The case of $R$ tending to zero

The result which we obtain for the interaction integrals when the radius (or the ratio of the radius to the box length) tends to zero is significant, since in this case  $C$  attains the values obtained in the "one-dimensional" AS FEMO scheme.

Previously (see I) the components of the interaction integrals were given in the form

$$\frac{1}{4} A_p^2 A_r^2 \int_0^L \int_0^L \cos a_p z \cos a_r z' \cdot \frac{e^2}{|z - z'|} dz dz' \quad (20)$$

which, however, was erroneous (see footnote 2), since the integrals of the (20)-type are divergent. Thus we have a case in which the integral of the limit, i. e.

$$\iint \lim_{R \rightarrow 0} \varrho(r) \varrho'(r') \cdot \frac{e^2}{|r - r'|} d\tau d\tau' \quad (21)$$

and hence, in view of normalization of  $\varphi$  in  $r, \vartheta$  variables, the integral (20)<sup>6,7</sup>, is not equal to the limit of the integral

$$\lim_{R \rightarrow 0} \iint \varrho(r) \varrho'(r') \cdot \frac{e^2}{|r - r'|} d\tau d\tau'. \quad (22)$$

In the latter case we obtain the results given in I. (See Appendix for the proof)<sup>8</sup>.

<sup>6</sup> We have assumed here, that the parts of  $\varphi$  depending on  $z$  have the more general form of the type  $A_z \sin a_z z$  ( $A_z$  is the normalization factor in  $z$ ). Then in  $C$  (see (6)) we have instead of  $\frac{1}{L^2}$  the factor  $\frac{1}{4} A_p^2 A_r^2$

<sup>7</sup> I am much indebted to Dr. H. Labhart for drawing my attention to the divergence of the integral (20).

<sup>8</sup> We obtain this result when for  $D$  we take the value  $2\pi$  in the  $C$  calculations of the present work. This corresponds to an equal distribution of the electron density about the box axis, hence to the assumptions of simple FE model.

The conclusions presented recently have interesting consequences from the point of view of classical electrostatics. This concerns to the problem of the interaction energy of charges in a very thin tube.

If we assume a priori, that the interaction potential in such a filament is of the type

$$\frac{1}{|z - z'|} \quad (23)$$

then after integration we obtain for the interaction energy a quantity tending logarithmically to infinity. On the other hand, when the problem is treated from the beginning as a three-dimensional one, and when with the result for the interaction energy we next pass to the limit for the cross-section tending to zero, we then obtain a finite value. For instance, in the case of two electrons moving freely in a filament of length  $L$ , the interaction energy attains  $\frac{e^2}{L}$ , e. g. the value of integral given in I in the case of  $c = a = 0$ .

This second interpretation of the calculation of the interaction energy seems to have stronger physical grounds.

### Appendix

It is essential to give the proof that as  $R \rightarrow 0$  the expressions obtained for the interaction integrals in the scheme developed above, go over into expressions obtained in the AS FEMO treatment (in I). Now let us perform those calculations for the simplest example:  $C$  in the case  $c = a = 0$ . The proof for other cases is quite similar.

We majorize by unity the Bessel functions appearing in the components of the  $C$  integral with minus signs (see Eq. (16) of this work). We shall show further that these integrals tend to zero for  $R \rightarrow 0$ .

In the first negative term we replace  $\tilde{\omega}$  by the series:

$$\tilde{\omega} = r_1 \sum_{m=0}^{\infty} C_m^{-1/2} (\cos \chi) \left( \frac{r_2}{r_1} \right)^m, \quad (r_2 < r_1) \quad (24)$$

where  $C_m^{-1/2}$  are Gegenbauer's coefficients of the expansion of  $\tilde{\omega}$ . After integration over  $r, r'$  we obtain for the first negative term the expression:

$$A \cdot \sum_{m=0}^{\infty} \sum_{k=0}^{\leq \frac{1}{2}m} \frac{(-1)^{k-1} 2^{m-2k-1} \Gamma\left(m-k-\frac{1}{2}\right)}{(m-2k)! k! \sqrt{\pi}} \cdot \frac{2}{m+2} \cdot \frac{R^5}{5} \int_0^{\pi} \cos^{m-2k} \chi d\chi \quad (25)$$

Integration over  $\chi$  gives quantities not larger than 2. The normalization product is proportional to  $R^{-4}$ , hence the whole expression is proportional to  $R$ . Thus it vanishes



when  $R$  tends to zero. Similarly the second negative term (with  $J$  equal unity) gives after integration (here, for  $a = 0$ , in  $M(\omega a)$  expansion we have  $m = n$ ):<sup>9</sup>

$$B \cdot \sum_{m=1}^{\infty} (-1)^m \frac{[2(m-1)]!}{(m!)^2 \cdot (2L)^{2m}} \sum_{k=0}^m \binom{m}{k}^2 \frac{1}{(2m-2k+2)(2k+2)} R^{2m+4} \quad (26)$$

( $A, B$  denote the constant factors in front of the integrals). Again taking the normalization factors into account, we find that the last expression is at least of the second order in  $R$ , and therefore also vanishes when  $R \rightarrow 0$ .

Thus there remains the first positive term in which the integration over  $r, r'$  with respect to the corresponding normalization coefficients of  $J$  functions gives simply unity. Taking all the factors into consideration we obtain  $C$  equal to  $\frac{e^2}{L}$ . This is identical with the value of  $C$  obtained for the same case in I (after dividing the latter by  $L^2$ , since in the previous definition of  $C$  the normalization factors of the functions depending on  $z$  were neglected).

#### КРАТКОЕ СОДЕРЖАНИЕ

С. Ольшевски, *Воздействие  $\pi$ -б в модели свободного электрона.*

Развито метод антисимметризованных молекулярных орбит в тримерной модели свободного электрона для линейных сопряженных молекул. Электроны  $\pi$  и  $\sigma$  создают газ в одном цилиндре растянутым вдоль цепи молекулы, а обе электронные группы схарактеризированы согласно с классификацией поданной Никитиным и Комоссом. Тогда полное воздействие  $\pi$  и  $\sigma$  может рассматриваться прямо, противоположно к подходу к этой проблеме в схеме Гепперт—Маер—Склар. Результаты на интегралы электронного воздействия в случае т. наз. одномерной модели свободного электрона, поданные автором в более ранней работе, были верифицированы как отвечающие интегралом полученным в сейчас рассматриваемой модели для случая когда радиус цилиндра приближается к нулю.

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<sup>9</sup> The term by term integration is permissible here in view of the uniform convergence of the integrated series.



## ON NUCLEAR MAGNETIC RESONANCE IN FLOWING LIQUID

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An investigation was made of nuclear magnetic resonance in a stream of flowing liquid. The dependence of the amplitude of the absorption lines on the rate of flow was investigated. It was established that the flowing liquid method allows a simultaneous determination of the saturation factor and the longitudinal relaxation time; in this connexion, the relaxation time measurement may be made for any (not too small) degree of saturation. It was also shown that the limit of applicability of the method can, in comparison with the limit of applicability given by Suryan, be shifted considerably in the direction of long relaxation times.

*Introduction*

Suryan (1951) made measurements of the amplitude of absorption lines of nuclear magnetic resonance in flowing liquid as a function of the rate of flow. If the following conditions are fulfilled:

a) the liquid, before entering the resonance coil, is in the magnetic field long enough for stationary magnetization  $M_0 = \chi_0 H_0$  to be attained, and b) the saturation of the resonance line is sufficiently strong<sup>1</sup>, it should be expected that there will be a linear increase of the line amplitude with an increase in the rate of flow

$$A = A_s \left( 1 + T_1 \frac{v}{l} \right) \quad (1)$$

where  $A$  is the observed amplitude of the resonance line for a rate of flow  $v$ ,  $A_s$  is the amplitude of the saturated line in the liquid at rest, and  $l$  is the length of the r. f. coil. Suryan obtained experimentally for a solution of N/1000  $\text{FeCl}_3$  in water a linear dependence of  $A$  on  $v$ , and from the slope of the straight line he determined  $T_1 = 0.06$  sec.

<sup>1</sup> Suryan gives the condition  $\frac{1}{2} \gamma^2 H_1^2 T_1 T_2^* \gg 1$ . Since the amplitude of modulation of the magnetic field  $H_m$  in his measurements is greater than the line width, this condition should have the form  $\gamma H_1^2 T_1 / H_m \gg 1$ .

The flowing liquid method allows a considerable improvement of the signal-to-noise ratio, which is of great importance in the case of small signals. For this reason, Denis et al. (1952), Bloom and Shoolery (1952), and Mitchell and Phillips (1956) used this method.

Gaussen (1955) used another method for measuring the time  $T_1$  by means of flowing liquid. The liquid, without previous magnetization, flowed through a resonance coil. After a sudden stopping of the flow it was observed that resonance lines arise as a result of the magnetization of the liquid which stopped in the coil. The recording of this process on film permitted the determination of  $T_1$ .

The flowing liquid method was used by Sherman (1954) to investigate nuclear magnetic resonance for separate regions of excitation and detection.

In this work, a more detailed investigation was made of the dependence of the amplitude of the resonance line on the rate of flow of the liquid in the stationary state. It was established that the flowing liquid method allows simultaneous determination of the saturation factor, and, in this connexion, the measurement of the relaxation time can be made for any value of this factor. It was also shown that the limit of applicability of this method can, in comparison with the limit given by Suryan, be shifted considerably in the direction of long relaxation times.

### *Simplified Theory*

The process of the saturation of samples by a high frequency field is discernable in the decrease of amplitude  $A$  of the absorption line and is described by the following equation:

$$A - A_s = (A_0 - A_s) e^{-\frac{t}{T_1 z}}, \quad (2)$$

where  $A_0$  is the initial amplitude of the line (at the moment the r. f. is applied),  $A_s$  is the amplitude of the line after saturation, and  $z = A_s/A_0$  is the saturation factor dependent on the amplitude of the r. f. field  $H_1$ , on the relaxation time  $T_1$  and on the amplitude of modulation of the magnetic field.

We denote

$$s = \frac{A - A_s}{A_s}. \quad (3)$$

The liquid flowing with a speed  $v$  flows through a coil of length  $l$  in a time  $t = l/v$ . We assume that before entering the resonance coil the liquid is in the magnetic field long enough for stationary magnetization  $M_0 = \chi_0 H_0$  to take place. The mean value of  $S$  for the region of the resonance coil is

$$s = \frac{1-z}{l z} \int_0^l e^{-\frac{x}{v T_1 z}} dx = \frac{v T_1 (1-z)}{l} \left( 1 - e^{-\frac{l}{v T_1 z}} \right). \quad (4)$$

There should be taken into account the velocity distribution of the liquid as a function of the distance  $r$  from the tube axis

$$v = 2\bar{v} \left[ I - \left( \frac{r}{R} \right)^2 \right], \quad (5)$$

where  $R$  is the tube radius and  $\bar{v}$  is the mean velocity of the liquid. The averaging over the cross section of the tube leads to an integral which cannot be evaluated analytically. It is sufficient, however, to restrict oneself to the examination of the limiting cases:

$$1. \quad \frac{l}{v T_1 z} \gg 1 \quad (6)$$

This condition corresponds to a slow flow of the liquid or to strong saturation. The neglecting in Eq. (4) of the term  $\exp(-l/v T_1 z)$  leads to the formula

$$s = (1 - z) \frac{\bar{v} T_1}{l} \quad (7)$$

$$2. \quad \frac{l}{v T_1 z} \ll 1 \quad (8)$$

This condition corresponds to a rapid flow or to weak saturation. Expanding  $\exp(-l/v T_1 z)$  into a series and neglecting terms of the order higher than one, we obtain

$$s = \frac{1 - z}{z} \quad (9)$$

The fulfilling of condition (8) may be in doubt, since the averaging over the tube cross-section gives a divergent integral. However, it is readily shown that this does not create any basic difficulty. For, integrating over the tube radius in the limits of from 0 to  $0.99R$ , and therefore, neglecting barely 0.2% of the volume of the flowing liquid, we obtain  $\left\langle \frac{l}{v T_1 z} \right\rangle_{av} \approx \frac{2l}{\bar{v} T_1 z}$ , which causes very little difficulty in satisfying condition (8).

The solution given leads to the conclusion that for a low rate of flow we have a linear dependence of  $s$  on  $\bar{v}$  while for sufficiently large rates of flow  $s$  ceases to depend on  $\bar{v}$  and attains a constant value  $s_s$ . The greater the coefficient  $z$ , and hence the weaker the saturation of the liquid in the stationary state the smaller the value  $\bar{v}$  for which the value  $s_s$  is attained. The line amplitude corresponding to the value of  $s_s$ , as may be seen from Eq. (9), is equal to  $A_0$ . Therefore, from the determined values of  $A_0$



and  $A_s$  we can calculate the saturation factor

$$z = \frac{A_s}{A_0} \quad (10)$$

and then, from the slope of the curve of  $A$  as a function of  $v$  we can calculate the relaxation time  $T_1$

$$T_1 = \frac{A - A_s}{A_s} \frac{l}{v(1 - z)} \quad (11)$$

A certain systematic error may be introduced by the fringing effect in the coil, owing to which the length is not precisely defined. This error, however, does not exceed a few percent, and in making the relative measurements, it was completely eliminated.

### *Equipment and Experimental Procedure*

The measurements were made for liquid containing protons by means of a bridge arrangement at a frequency of 28 Mc/sec in a magnetic field of 6,580 Oe. The electro-magnet used had a pole face diameter of 140 mm and a gap width of 30 mm. An energizing current of 5.4 A was supplied by an accumulator battery. By means of three differential screws which allowed the pole faces to be adjusted precisely parallel to one another a change in the magnetic field of  $\Delta H < 0.02$  Oe was obtained in a region of the sample 15 mm in length and 7 mm in diameter. The block diagram of the equipment is shown in Fig. 1. An r. f. bridge of the double — T type given by Grivet

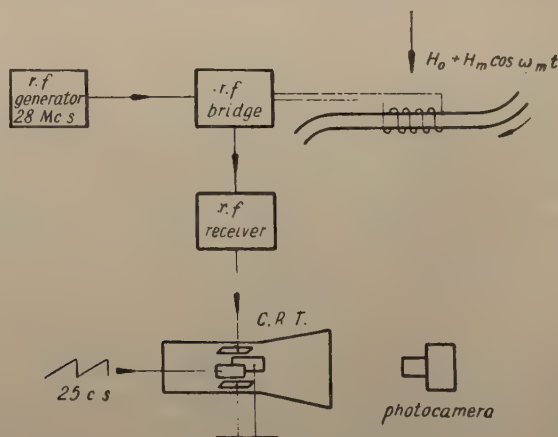


Fig. 1. Block diagram of the equipment

et al. (1951) was used. The liquid flowed through a glass tube, the inner diameter of which was accurately measured. On the tube was wound the r. f. coil. Before entering the coil, the liquid flowed through a helical tube placed between the pole pieces

of the electromagnet. This allowed the stationary value of magnetization to be attained (Fig. 2). The length of the path of the liquid in the magnetic field was 360 cm. or, with a flow of 40 cm/sec, the mean time spent by the liquid in the magnetic field was 9 sec. This time, which in the case of water is 3.5 times longer than the relaxation time, was sufficient, in practice, for the full value of  $M_0$  ( $M = 0.97 M_0$ ) to be attained. In the case of a liquid with a shorter relaxation time, the magnetization was still closer

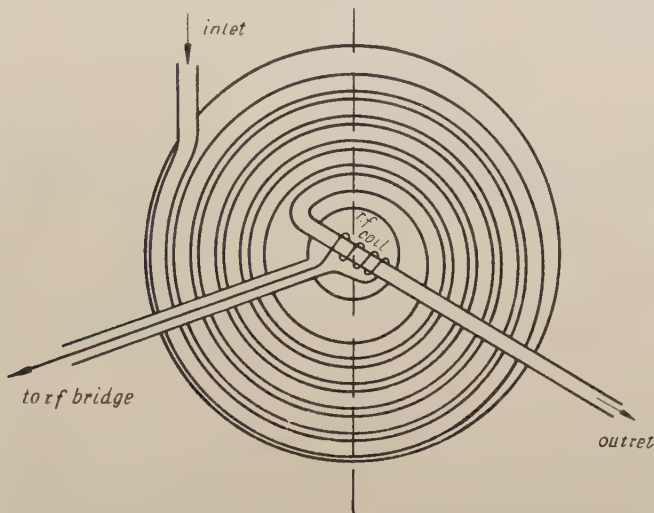
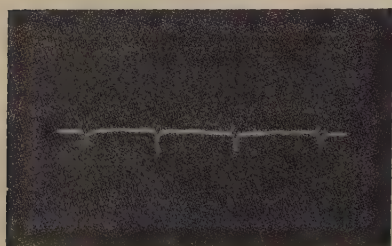
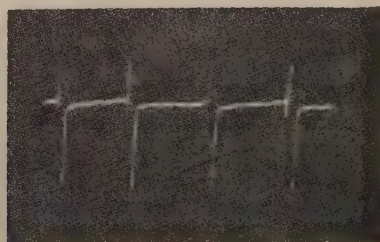


Fig. 2. Path of liquid between pole faces of the electromagnet

to the value  $M_0$ . The liquid flowed under a pressure of about 0.25 atm from a reservoir placed under the ceiling of the laboratory. In order to facilitate the change of the rate of flow a set of 20 capillary tubes with suitably chosen diameters was used. These were placed at the outlet of the liquid stream. The capillary tubes were calibrated by accurately measuring the rate of flow for each. Such set of capillary tubes considerably facilitated the experimental procedure, since the measurements could be repeated several times in short intervals of time without the necessity of making each time



a



b

Fig. 3. Photograph of resonance line of distilled water for different rates of flow a)  $\bar{v} = 0.5$  cm/sec  
b)  $\bar{v} = 40$  cm/sec.

a time-consuming measurement of the rate of flow. For various rates of flow the absorption lines were photographed from the oscillograph screen. In Fig. 3 are shown sample photographs of absorption lines in distilled water for two different rates of flow. In order to avoid the influence of any eventual detuning of the bridge, high-frequency generator, or receiver, every second measurement was made for a standard capillary tube and the line heights as measured from the photographs were referred to the line heights for this capillary.

### Results of the Measurements

Several series of measurements were made for ordinary distilled water and for an  $n/1000$  solution of  $\text{MnSO}_4$  in water. For both liquids measurements were made for two different values of the high-frequency field, and hence, for different saturation factors.

Figs. 4 and 5 show curves of the line amplitudes as a function of the rate of flow of the liquids. The shape of the experimental curves fully confirm the theoretical

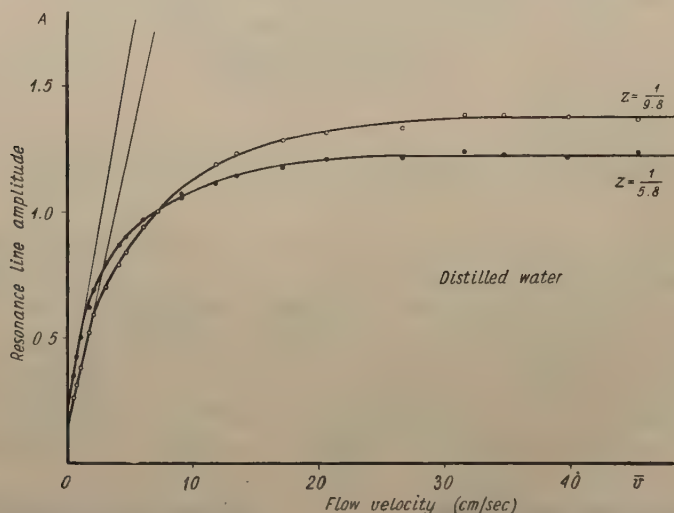


Fig. 4. Plot of amplitude of resonance line vs rate of flow for distilled water

predictions. From the curves drawn on the basis of Eqs. (10) and (11) the saturation factors and the longitudinal relaxation times were calculated. The following values were obtained:

Distilled water

$H_1$ lower	$Z = 1/5.8$	$T_1 = (2.60 \pm 0.20) \text{ sec}$
$H_1$ higher	$Z = 1/9.8$	$T_1 = (2.77 \pm 0.25) \text{ sec}$

1/1000 n  $\text{MnSO}_4$  solution

$H_1$  lower  $Z = 1/2.2$   $T_1 = (0.246 \pm 0.20)$  sec

$H_1$  higher  $Z = 1/3.0$   $T_1 = (0.257 \pm 0.20)$  sec

The errors listed were estimated on the basis of the accuracy with which the values of  $A_0$ ,  $A_s$  and the slope of the linear portions of the curves may be read.

The results of this work show that the flowing liquid method can be used for measuring the relaxation time also when the saturation is not large, since the line

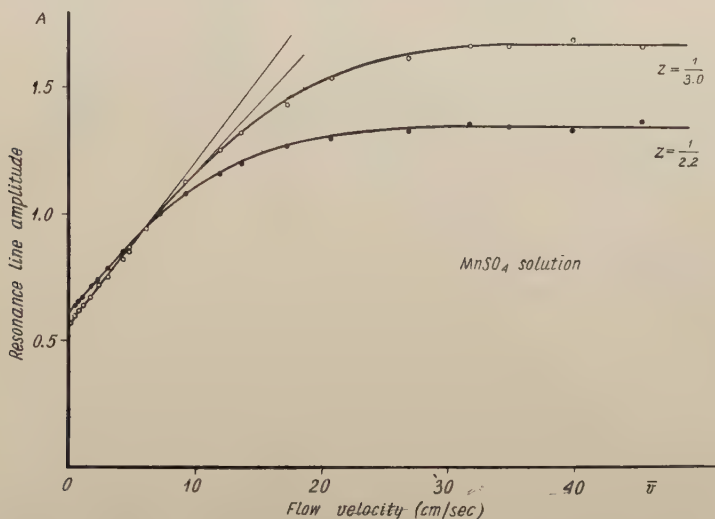


Fig. 5. Plot of amplitude of resonance line vs rate of flow for n/1000 solution of  $\text{MnSO}_4$  in water

amplitude measurement for high rates of flow permits the direct determination of the saturation factor. As may be seen from the example of distilled water, the method described can be used for measuring long relaxation times of the order of seconds.

We would like to thank Professor H. Niewodniczański for making this work possible in his laboratory and K. Krynicki and G. Zapalski for valuable aid in making the measurements.

#### КРАТКОЕ СОДЕРЖАНИЕ

А. Грынкевич и Т. Валюга, *Ядерный магнитный резонанс в текущей жидкости*

Проведено исследование ядерного магнитного резонанса в текущей жидкости. Определено зависимость амплитуды линии абсорбции от скорости течения. Доказано что метод текущей жидкости позволяет одновременно получить коэффициент насыщения и продольное время релаксации и поэтому измерение времени релаксации можно исполнить при любой (не слишком малой) степени насыщения. Показано тоже что предел измеряемых этим методом времен релаксации по сравнению с пределом поданным в работе Сурияна можно значительно расширить в направлении длинных времен.

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## INVESTIGATION OF OPERATING CONDITIONS OF A DIELECTRIC RESONANT AMPLIFIER

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The authors investigated the operating conditions of a dielectric resonant amplifier and the dielectric properties of  $(\text{Ba-Sr})\text{TiO}_3$  ferroelectric condensers employed in the amplifier. Curves of the relative permittivity variation *versus* the *DC* field at various temperatures were obtained. The following characteristics of the dielectric amplifier under investigation were measured: output voltage *versus* signal voltage and signal frequency, and voltage amplification coefficient *versus* temperature. The largest voltage amplification value was obtained within the Curie point region. The temperature being constant, this amplification value remained practically constant over the entire audio frequency range. The measurements proved that it is possible to determine the optimal operating conditions of the dielectric amplifier from the graphs showing the dependence of the permittivity of the ferroelectric material on the *DC* field and on the temperature.

### *Introduction*

During recent years a number of papers (Vincent, 1951, Pipes, 1952, Urkowitz, 1952, Penney et al. 1953, Silverstein, 1954, Mason and Wick, 1954) have been published on the use of ferroelectric materials as nonlinear elements in dielectric amplifiers. Since the results hitherto published are insufficient for determining the optimum operating conditions of an amplifier, the authors submitted the dielectric properties of ferroelectric materials employed in amplifiers, and the operating characteristics of dielectric resonance amplifiers, to a detailed investigation.

### *1. Preparation of ferroelectric material*

The ferroelectrics investigated were obtained from solid  $(\text{Ba-Sr})\text{TiO}_3$  solutions by known methods (Trzebiatowski et al. 1952). The authors prepared a number of series of ferroelectrics varying in Sr content, starting from chemically pure  $\text{BaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{TiO}_2$ , which after being mixed, were sintered for 3 hours at  $1300^\circ\text{C}$ . The  $(\text{Ba-Sr})\text{TiO}_3$  thus obtained was ground and subsequently compressed into disks

12 mm in diameter under pressures of 5 — 8 t/cm<sup>2</sup>. The disks were then sintered once more for 2 hours at 1200°C and 3 hours at 1350°C consecutively, yielding material of low porosity. After the disks had been polished down to a thickness of 0.15—0.20 mm, the surfaces were covered with silver electrodes by evaporating in vacuo.

## 2. Measurements of field and temperature dependence of the dielectric permittivity in (Ba—Sr) TiO<sub>3</sub>

The dielectric permittivity in polycrystalline (Ba—Sr)TiO<sub>3</sub> falls with growing field bias (Piekara and Pająk, 1953). Using the circuit shown in Fig. 1 it could be proved that the conditions prevailing during operation of a dielectric amplifier are the following: as the signal voltage increases, the dielectric permittivity of (Ba—Sr)TiO<sub>3</sub> decreases, and conversely, during the period of decreasing of the signal voltage the permittivity increases. Low frequency signals from an audio generator were supplied

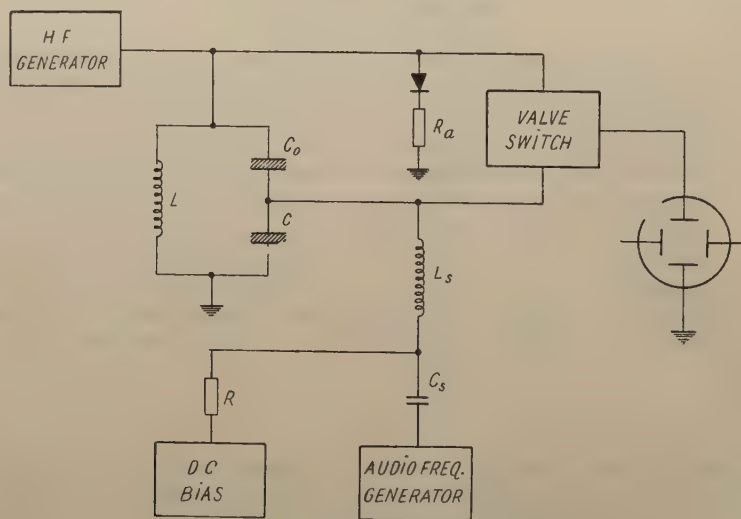


Fig. 1 Dielectric resonance amplifier circuit.

to the dielectric amplifier, changing the capacitances of polarized ferroelectric condensers in the resonant amplifier circuit and thus causing the latter to detune. The amplifier signals and the low-frequency generator signals were supplied to the oscillograph over a valve switch. Thus, the output and input signals were observed simultaneously. In order to ascertain whether the changes in the permittivity of (Ba—Sr)TiO<sub>3</sub> caused by momentary changes in the signal voltage supplied to the amplifier are the same as those caused by a DC voltage, the permittivity was measured as a function of DC voltages at various temperatures. The capacitance of the ferroelectric elements of the amplifier was measured by the bridge method at a frequency of 2 kc/s and a measuring field of 10 V/cm.

The results are plotted in Figs. 2 and 3. The curves show the effect of the applied field on the relative permittivity  $\frac{\Delta\epsilon}{\epsilon}$  at various fixed temperatures, and the permittivity — temperature dependence at various values of the field intensity. It will be noticed that the field causes the greatest changes in the vicinity of the Curie point. It will be shown, that, indeed, in order to obtain maximum amplification, the Curie

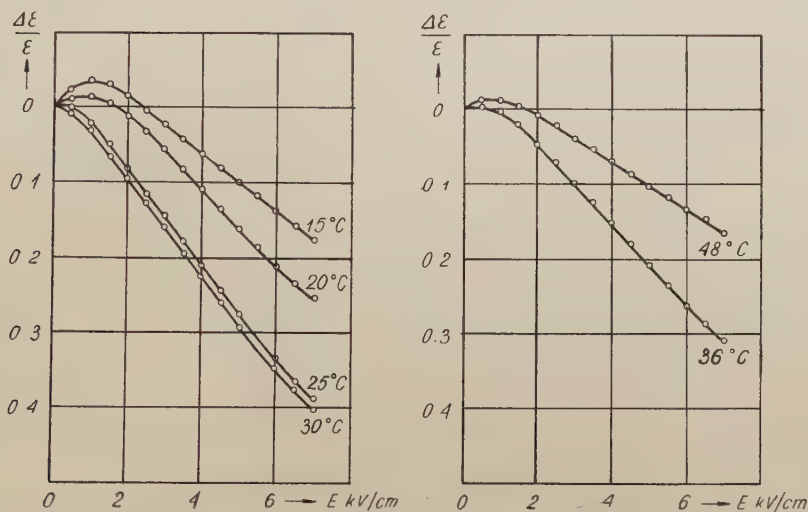


Fig. 2 Relative dielectric permittivity of (Ba—Sr)TiO<sub>3</sub> versus biasing field at various constant temperatures

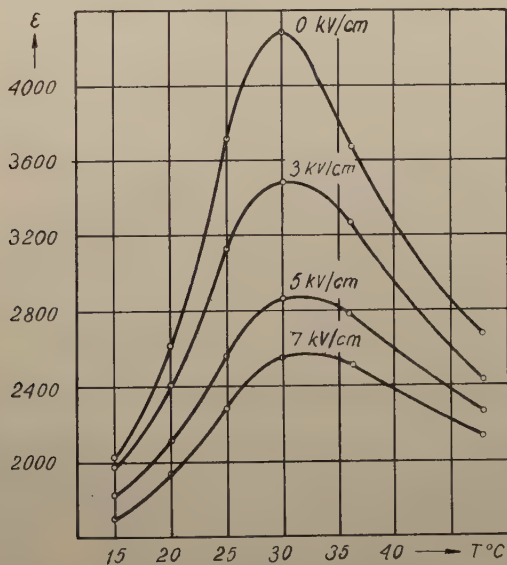


Fig. 3 Dielectric permittivity of (Ba—Sr)TiO<sub>3</sub> as function of the temperature at various biasing fields.

temperature of the ferroelectric condensers employed should not differ considerably from the operating temperature.

The curves plotted in Fig. 2 show identical slope in the vicinity of the Curie point ( $30^{\circ}\text{C}$ ). Within this range of temperature, amplification is independent of temperature changes in the operating conditions of the amplifier. The maximum steepness near the Curie point ( $25^{\circ}\text{C} - 36^{\circ}\text{C}$ ) is about 0.07 per 1 kV/cm, and falls to 0.06 per 1 kV/cm between  $20^{\circ}\text{C} - 25^{\circ}\text{C}$  and  $36^{\circ}\text{C} - 45^{\circ}\text{C}$ . The ratio of these two values is 0.85, corresponding to 1.42 dB relative amplification units, which practically lies below the threshold of perceptibility in an audio amplifier. Operating conditions of a dielectric amplifier are considerably worse at temperatures more distant from the Curie point. For example, a change in temperature from  $15^{\circ}\text{C}$  to  $20^{\circ}\text{C}$  corresponds to a loss of the relative amplification of 4.1 dB, which is sufficient to be perceptible.

### 3. Operating characteristics of the (Ba—Sr) $\text{TiO}_3$ dielectric amplifier

The resonance amplifier was constructed according to Fig. 1. The ferroelectric condensers  $C_0$  in the resonant circuit were polarized over the resistance  $R$  by employing a DC field of 3 to 5 kV/cm; within this range  $\mu = \frac{1}{\epsilon} \frac{\Delta\epsilon}{\Delta E}$  is constant. The frequency of 580 kc/s which was applied to the amplifier was chosen so as to provide for operation

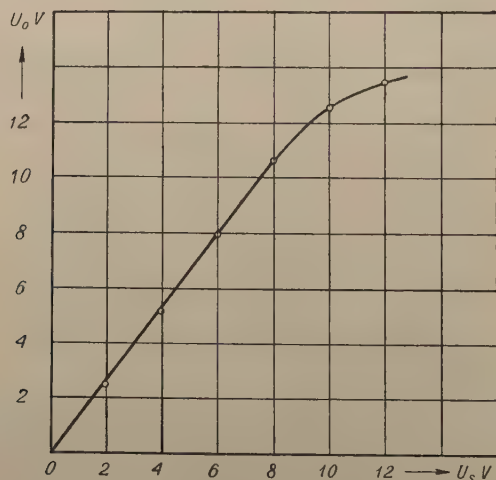


Fig. 4 Output voltage  $U_o$  as function of the signal voltage  $U$ .

on the resonance curve slope of the  $LC$  circuit. Audio signals of a frequency of 0 — 20 kc/s were fed to the coupling condenser  $C_s$  and the  $HF$  filter  $L_s$ . The  $LF$  and  $HF$  voltages were measured with a valve voltmeter and a scaled oscillograph, respectively. The following characteristics of the dielectric amplifier under investigation were investigated:

1. Output voltage *versus* signal voltage and signal frequency,
2. Voltage amplification coefficient *versus* temperature.

Measurements of output voltage *versus* signal voltage (Fig. 4) with the resonant amplifier operating in the vicinity of the Curie point ( $30^{\circ}\text{C}$ ) yielded the maximum value of the voltage amplification coefficient  $k = \frac{U_0}{U_s} = 1.3$ .

It was found that the output voltage is independent of the signal frequency within the audio frequency range investigated (continuous curve in Fig. 5). From measure-

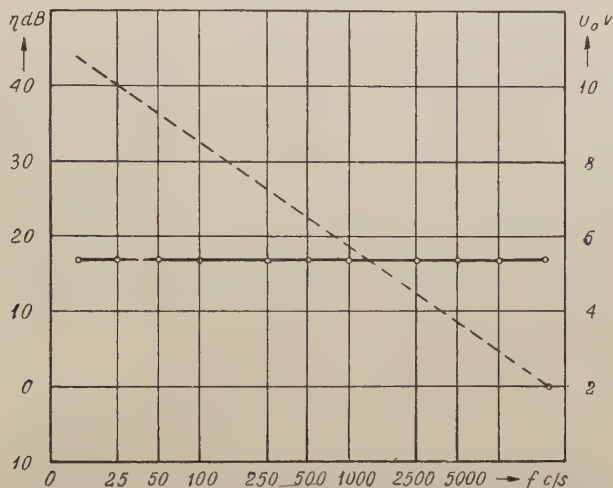


Fig. 5 Output voltage  $U_0$  and power gain coefficient  $\eta$  as function of the signal frequency.

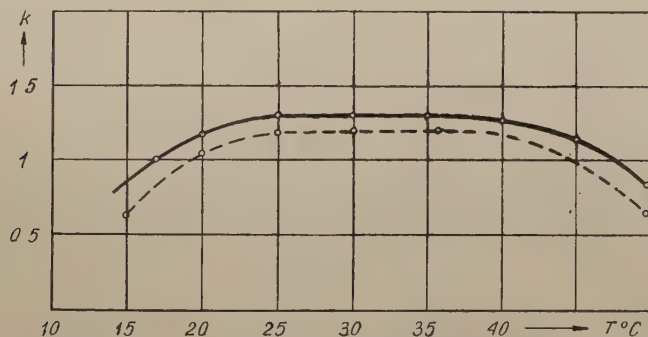


Fig. 6 Voltage amplification coefficient  $k$  of the amplifier shown in Fig. 1, as a function of the temperature. Dashed curve: the coefficient  $k$  calculated from eq. (3), with the value of  $\mu$  obtained from the slope of the static characteristics shown in Fig. 2.

ments of the signal voltage, output voltage and also input and output impedances, the power gain coefficient  $\eta$  was calculated. This power gain coefficient was plotted



versus frequency (dashes in Fig. 5). The maximum power gain within the  $LF$  range amounted to about 40 dB.

The temperature dependence of the voltage amplification coefficient  $k$  is shown in Fig. 6 (continuous curve). It will be noticed that maximum voltage amplification occurs in the vicinity of the Curie point ( $30^\circ\text{C}$ ). Variations in temperature amounting to  $5^\circ\text{C}$  —  $10^\circ\text{C}$  when operating near the Curie point produce changes in the amplification coefficient so restricted as to be practically negligible. However, a considerable decrease of  $k$  appears when the amplifier operates at temperatures remote from the Curie point. The authors explain this decrease in the amplification coefficient by the fact that the largest transient variations of the permittivity of the ferroelectric material appear within the region of the Curie point. Hence, the Curie temperature of the ferroelectric material employed should lie in the proximity of the operating temperature of the amplifier. Similarly, the largest variations of the permittivity of the ferroelectric material are caused by a biasing  $DC$  field near the Curie point (Fig. 2 and 3).

The dashed curve in Fig. 6 shows the temperature dependence of the voltage amplification coefficient  $k$  calculated according to the theory of H. Urkowitz (1952), using  $\mu$  obtained from the static measurements (Fig. 2 and 3). The change of the  $HF$  amplitude voltage  $U_0$  as function of the signal amplitude  $U$  (eq. 39 in his paper), using our notations, is given by:

$$U_0 = 0.1 I R Q \omega^2 L C' \left( \frac{\mu}{s} \right) U, \quad (1)$$

where  $I$  is the constant amplitude of the  $HF$  current,  $R$  — the resistance of the circuit,  $Q$ ,  $L$ ,  $C'$  — resonance circuit constants,  $\mu = \frac{1}{C'} \frac{dC'}{dE_s}$ ,  $s$  — the thickness of each of the ferroelectric condensers;  $C'$  denotes the capacity seen by the signal. Denoting the capacity of the resonance circuit seen by the  $HF$  generator by  $C$ , we obtain  $C' = 4 C$ . The voltage amplification coefficient is now:

$$k = \frac{U_0}{U_s} = 0.4 I R \omega^2 L C \left( \frac{\mu}{s} \right) \quad (2)$$

In this equation  $\omega^2 L C \cong 1$ . For optimal conditions  $I R = U \sqrt{3/2}$ , where  $U$  is the amplitude of the  $HF$  voltage. Denoting  $\frac{U}{2s} = E_0$  we have for the voltage amplification coefficient:

$$k = 0.96 E_0 \mu Q \quad (3)$$

where  $E_0$  denotes the  $HF$  field strength in  $\text{kV/cm}$ ,  $Q$  — the figure of merit of the resonant circuit and  $\mu = \frac{1}{\epsilon} \frac{d\epsilon}{dE_s}$  in  $\text{cm/kV}$ . The values of  $\mu$  for various temperatures are calculated from the curves given in Fig. 2 with  $DC$  fields of 3 to 5  $\text{kV/cm}$ . For the amplifier investigated  $E_0$  amounted to 0.75  $\text{kV/cm}$  and  $Q = 22.8$ . On comparing both

curves it will be seen that the variations of the permittivity of the ferroelectric material induced by the  $AC$  field of audio frequency, with a  $DC$  field superimposed on it, are almost the same as the variations of the reversible permittivity caused by a  $DC$  field (Fig. 2). As both curves in Fig. 6 are approximately parallel, it is thus possible to determine the optimal operating conditions of the amplifier from the  $DC$ -field-permittivity and the temperature-permittivity dependence of the ferroelectric material. As follows from the graphs in Fig. 6 the error in determining the voltage amplification coefficient by this method does not exceed about 8%.

### Conclusions

The dielectric resonance amplifier yields the largest voltage amplification (however, only slightly exceeding 1) when operating within the region about the Curie point. The temperature being constant, the amplification remains practically constant over the entire audio frequency range.

The optimal operating conditions for the dielectric amplifier may be determined from the curves showing the effect of the  $DC$ -field and of the temperature on the permittivity of the ferroelectric material.

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### КРАТКОЕ СОДЕРЖАНИЕ

Т. Краевский, Е. Петржак и Я. Сувальский, *Исследование по рабочим условиям диэлектрического резонансного усилителя.*

Авторы провели исследования по рабочим условиям диэлектрического резонансного усилителя и диэлектрическим свойствам сегнетоэлектрических конденсаторов содержащих  $(\text{Ba-Sr})\text{TiO}_3$ , применяющихся в усилителе. Определены кривые зависимости  $\Delta\epsilon/\epsilon$  от напряженности постоянного поля для различных температур. Для исследуемого усилителя определялись: зависимость напряжения на входе от напряжения и частоты сигнала и температурная зависимость коэффициента усиления напряжения. Максимальное усиление напряжения появлялось в области точки Кюри; для данной температуры оно оказалось практически постоянной величиной во всём акустическом диапазоне. Результаты измерений производившихся авторами приводят к заключению, что оптимальные рабочие условия диэлектрического усилителя определены на основании хода зависимости диэлектрической проницаемости сегнетоэлектрического материала от напряженности постоянного электрического поля и от температуры.

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